Reactions of Unsaturated Azides, 6[1]

Synthesis of 1,2,3-Triazoles from Propargyl Azides by Rearrangement of the Azido Group. – Indication of Short-Lived Allenyl Azides and Triazafulvenes

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Treatment of 3-bromo-3-methyl-1-butyne (**1**) or 1-iodo-3-methyl-1,2-butadiene (**3**) with solutions of sodium azide affords 3-azido-3-methyl-1-butyne (**5**) which reacts already at room temperature to 1,2,3-triazoles **8**–**11**. Structures of **5** and **8**–**11** are verified by independent syntheses and spectroscopic data although in part other assignments of structures have been published. The preparation of 1*H*-1,2,3-triazoles via propargyl azides is carried out in the presence of various nucleophiles and investigated by means of ^{15}N-labelled starting material as well as optically active 3-azido-1-butyne (*R*-**21**). The only mechanism compatible with all results includes short-lived allenyl azides and triazafulvenes. Thus, propargyl azide **14** rearranges to allenyl azide **16** leading to triazafulvene **18** by rapid ring closure. Finally, **18** is trapped by nucleophiles to give triazole **17**. The conversion of various propargyl compounds into *N*-unsubstituted 1*H*-1,2,3-triazoles **23**, **41**, **44**, **46**, **50**, and **51** is effected by a one-pot procedure without isolation of **14** and turns out to be a convenient method to prepare these heterocycles.

Reaktionen ungesättigter Azide, 6[1]. – Synthesen von 1,2,3-Triazolen aus Propargylaziden durch Umlagerung der Azid-Gruppe. – Hinweise auf kurzlebige Allenylazide and Triazafulvene

In Natriumazid-Lösungen setzen sich 3-Brom-3-methyl-1-butin (**1**) oder 1-Iod-3-methyl-1,2-butadien (**3**) zu 3-Azido-3-methyl-1-butin (**5**) um, das schon bei Raumtemperatur zu den 1,2,3-Triazolen **8**–**11** weiterreagiert. Unabhängige Synthesen und spektroskopische Charakterisierungen belegen die Strukturen von **5** und **8**–**11**, für die in der Literatur teilweise andere Strukturzuordnungen getroffen worden sind. Die Darstellung von 1*H*-1,2,3-Triazolen über Propargylazide wird in Gegenwart verschiedener Nucleophile durchgeführt und mit Hilfe ^{15}N-markierter Edukte sowie unter Einbeziehung von optisch aktivem 3-Azido-1-butin (*R*-**21**) untersucht. Mit allen Ergebnissen ist nur ein Mechanismus über kurzlebige Allenylazide und Triazafulvene im Einklang. Demnach lagert sich Propargylazid **14** zu Allenylazid **16** um, das durch raschen Ringschluß zu Triazafulven **18** führt; dieses wird durch Nucleophile zum Triazol **17** abgefangen. Die Reaktion diverser Propargyl-Verbindungen zu den *N*-unsubstituierten 1*H*-1,2,3-Triazolen **23**, **41**, **44**, **46**, **50** und **51** kann als Eintopf-Verfahren ohne Isolierung von **14** durchgeführt werden und erweist sich damit als eine bequeme Synthesemethode für diese Heterocyclen.

Vinyl azides which are known for their manifold reactions can be synthesized by various methods[2]. But all attempts to isolate allenyl azides – possible precursors for yet unknown alkylideneazirines – were unsuccessful[3,4]. In a publication by Shiner and Humphrey, the authors claimed to have obtained the allenyl azide **4** together with the propargyl azide **5** from the reaction of bromides **1** or **2** with sodium azide in deuterated aqueous ethanol[5]. However, **4** and **5** were only characterized in the reaction mixture by their ^1H-NMR data, because they decomposed already at room temperature to unknown products. Since the observation of **4** represents the only direct reference to an allenyl azide, detailed reinvestigations of the reaction of **1** with sodium azide in aqueous alcohols are now presented.

1,2,3-Triazoles from 3-Azido-3-methyl-1-butyne (5)

Treatment of **1**[6,7] with sodium azide in aqueous ethanol at first gives only the propargyl azide **5**, which subsequently produces the triazoles **8**–**10**[8], along with the other solvolysis products, 2-methyl-1-buten-3-yne, 2-methyl-3-butyn-2-ol, and **12**. NMR data indicate that **9** was taken for **3** in the literature, that **5** was correctly recognized, and that **8** and **10** are the succeeding products not identified by Shiner and Humphrey[5]. If the reaction is carried out using deuterated solvents the allenyl azide **4** cannot be detected by ^1H-NMR spectroscopy. With sodium azide in aqueous methanol, **1** or the less reactive **3**[7,10] similarly furnish **5** and subsequently **8**, **9**, and **11**. Due to the formation of several solvolysis products the triazoles are isolated in low yields (16% of **9** and 16% of **11** based on **1**). Using sodium azide in aqueous acetone affords only **8** and **9** as final triazoles (43% yield based on **1**). Although the azide **5** is very unstable at room temperature it can be isolated from **3** and hexadecyltributylphosphonium azide (QN_3)[11] in 44% yield. With sodium azide in aqueous alcohols, **5** produces **8** and **9** as well as **10** or **11**. Using ^{15}N-labelled sodium azide in aqueous methanol the label is found only in the azido group of **9** but not in the triazole part of **9** or **11**. This result excludes "simple azide cycloaddition"[3] to give triazoles. Moreover, **13** is quite stable in the presence of sodium azide in aqueous

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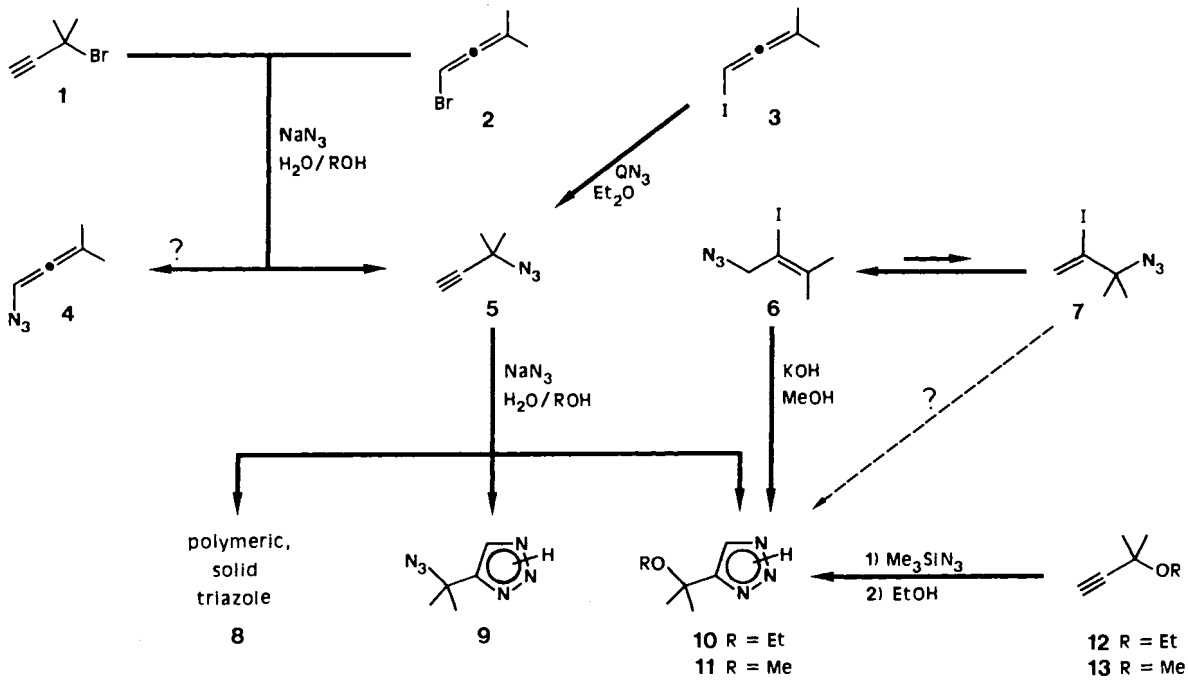
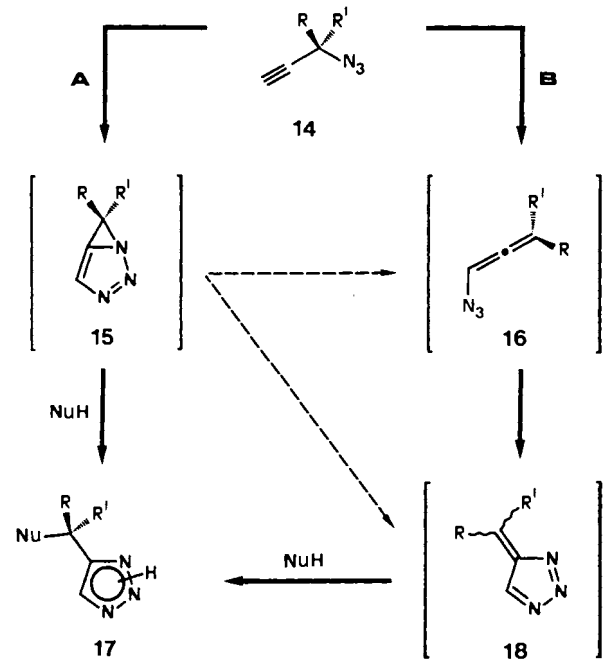


methanol and does not lead to any triazole by cycloaddition[12]. In aqueous methanol (without sodium azide), **5** affords exclusively **11**, while only **8** is found without nucleophiles, e. g. if **5** is decomposed in chloroform solution. Treatment of **6**[4] with potassium hydroxide in methanol produces **11** in a slow reaction. Starting with the ethers **12**[14] or **13**[15], the triazoles **10** and **11** can be synthesized independently with 39% or 54% yield, respectively. For that purpose the ethers are treated with trimethylsilyl azide in a 1,3-dipolar cycloaddition, and the silyl groups are removed by ethanol[16].

Mechanisms for the Conversion of Propargyl Azides to 1,2,3-Triazoles

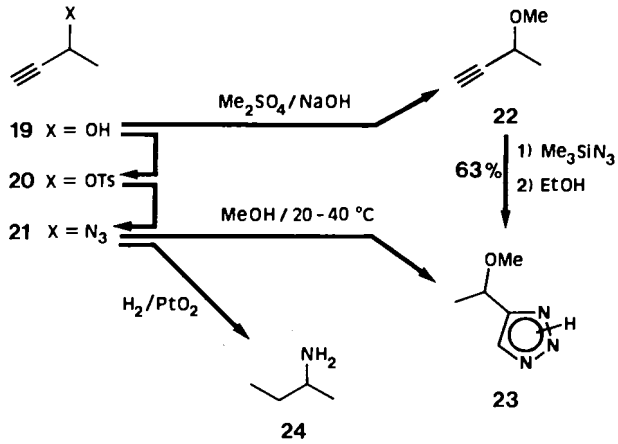
According to the transformation of propargyl azides to 1,2,3-triazoles, the experimental results can be rationalized by two different reaction mechanisms: pathway A starts with an intramolecular 1,3-dipolar cycloaddition of the azido group of **14** to the C–C triple bond[17]. A nucleophile NuH, e. g. methanol, would attack the resulting very strained triazole **15**[18] with inversion yielding **17**. Path B supposes at first a rearrangement **14** → **16** which possibly takes place as a triaza Cope rearrangement[19]. The unstable allenyl azide **16** cyclizes to triazafulvene[20] **18** generating **17** by the reaction with the nucleophile NuH. Using optically active **14**, total racemization will only be found if the reaction takes path B via the planar **18**. Path B is not the only way for the conversion of **6** to **11** using potassium hydroxide in methanol (**6** → **4** → **16** → **18** → **11**). Since **6** and **7** can undergo equilibration by [3.3] rearrangement[4], path A (**6** ⇄ **7** → **5** → **15** → **11**) is also possible.

Using propargyl azide **21**, path A and B to triazoles can be differentiated: If tosylate **20**[21] is treated with lithium or sodium azide in methanol the formed azide **21** is converted exclusively to **23** in the presence of pure methanol (82% yield referred to **20**). In chloroform solution, **21** which can be isolated from **20** and QN_3 with 82% yield decomposes to polymeric material[22]. The structure of **21** is confirmed not only by spectral data but also by the hydrogenation to **24**. **23** is also synthesized from ether **22**[24].

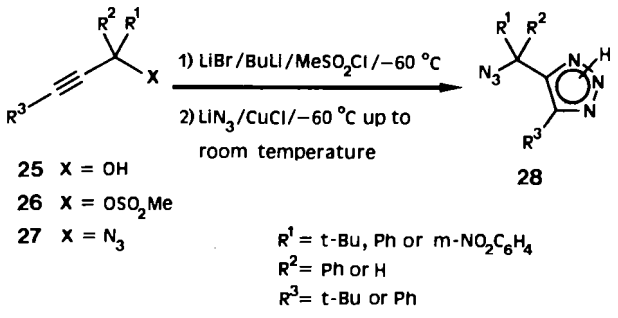


S-**20** prepared from *S*-(−)-**19** (83% ee)[25] can be converted to *R*-**21**. With methanol this optically active propargyl azide furnishes the triazole **23** with > 99.97% racemization. Hydrogenation of *R*-**21** to the known *R*-(−)-**24**[26] indicates the optical activity of the azide. If *S*-(−)-**19** is transformed[24] to *S*-**22** and subsequently treated with trimethylsilyl azide the resulting *S*-(−)-**23** shows a high rotation value. These results

demonstrate that propargyl azides most likely lead to 1,2,3-triazoles via allenyl azides and achiral triazafulvenes as short-lived intermediates (path B). Other routes (dashed lines) may be considered, but they are less likely. Further studies (publication submitted) will demonstrate that allenyl azides act as precursors of triazafulvenes and 1,2,3-triazoles.

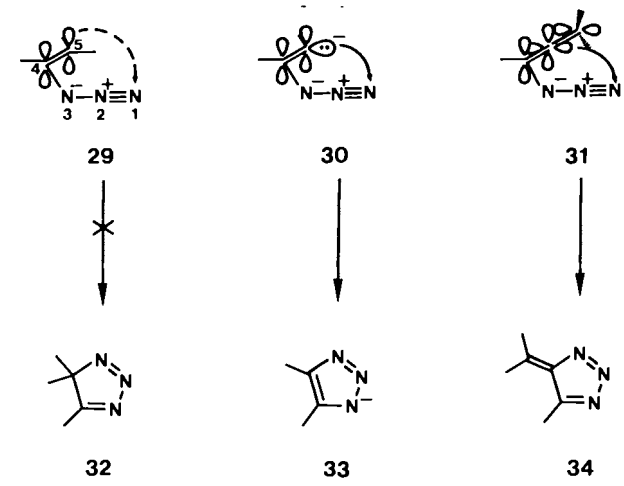


Pathway B may also explain the conversion of alcohols **25** to triazoles **28** (yield 6–24%) described by L'abbé and co-workers[3]. The authors postulated a reaction via intermediates **26** and **27** (compare **19** → **20** → **21** → **23**). But it is *not* "obvious that a direct displacement reaction coupled with azide cycloaddition has occurred and that no allenyl azide is involved" [3]. A more complex mechanism like pathway B may explain the transformation of *R*-**21** to completely racemic **23** (Nu = OMe) as well as the conversion **27** → **28** (Nu = N_3).



In the absence of nucleophiles propargyl azides (e.g. **5** and **21**) tend to polymerize. For 3-azido-1-propyne (**49**), polymerization is explained by intermolecular 1,3-dipolar cycloaddition[23,27]. In spite of steric hindrance by additional methyl groups polymerization of neat **5** or of **5** in chloroform solution is much more rapid than that of **49**. This result excludes polymerization of **5** by simple intermolecular 1,3-dipolar cycloaddition. Rate-determining rearrangement[28] **5** → **4** and subsequent cyclization to **18** (R = R′ = Me) which polymerizes in the absence of nucleophiles may explain the low stability of **5**. In the presence of weak nucleophiles like water, **18** can be attacked by **17** competitively leading to oligomeric and polymeric triazoles.

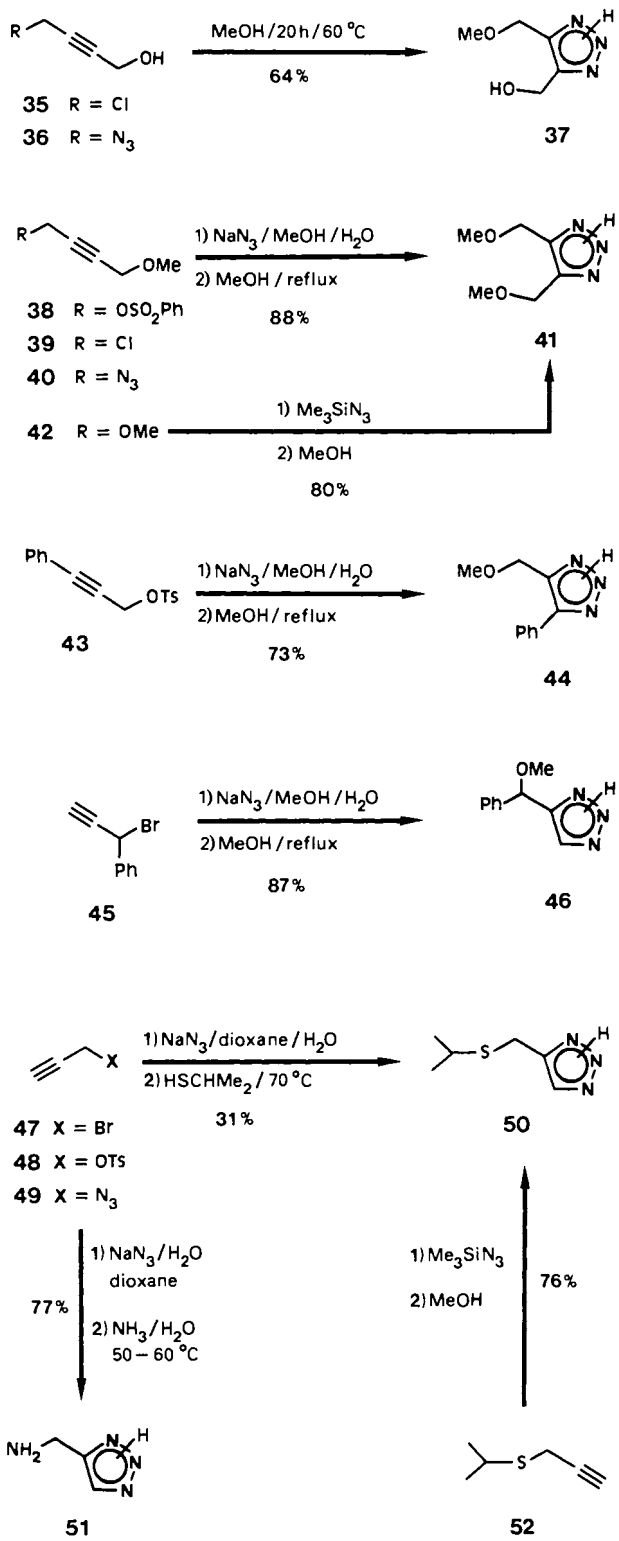
Ring closure of vinyl azides **29** to 4*H*-1,2,3-triazoles **32** has been studied by ab initio calculations[29] and has been discussed to be the first step for the transformation of **29** to 2*H*-azirines[30]. The cyclization **29** → **32** has been found only in the case of α-azidoenamines[31], but simple vinyl azides do not give 1,2,3-triazoles by intramolecular reaction[32]. Poor nucleophilicity at C-5 of **29** or unfavourable geometry (distance between the orbitals of N-1 and C-5) may be the reason why simple vinyl azides do not cyclize to **32**. The possibility of ring closure is more favourable in the case of carbanion **30**, and the conversion to **33** is known to be a rapid isomerization[33]. Advantageous geometry (two perpendicular p orbitals of the central carbon atom) possibly causes the fast cyclization of allenyl azide **31** to triazafulven **34**.



A Novel Method for the Synthesis of 1,2,3-Triazoles via Propargyl Azides

Starting with propargyl azides other 1,2,3-triazoles can be obtained. The azide **36** synthesized from **35**[34] (yield 73%) furnishes the heterocycle **37** in methanol solution, whereas heating in chloroform solution gives only polymeric material. One-pot conversion of **38**[35] into **41** proves to be favourable since isolation of the potentially unstable and explosive azide **40** is avoided. For that purpose a small excess of **38** (or **39**[36]) is treated with sodium azide at room temperature. The resulting solution of **40** yields **41** after treatment with refluxing methanol (88% referred to sodium azide). **41** is also obtained from **42**[37] using 1,3-dipolar cycloaddition with trimethylsilyl azide. Starting with **43**[38], an analogous one-pot synthesis furnishes **44**. The course of the first step and the complete consumption of sodium azide can be observed conveniently by measurement of the decreasing pH. The bromide **45**[39] is converted to **46** by a similar one-pot procedure.

Synthesis of 1,2,3-triazoles via propargyl azides is not restricted to nucleophiles like azide ion and alcohols. Other nucleophiles (NuH for the step **18** → **17**) may be used. If a small excess of **47** is treated with sodium azide, the resulting solution of **49** reacts with 2-propanethiol to yield **50** which is also prepared starting with **52**[40]. The one-pot conversion of **48**[21a] to **51** using the nucleophilicity of ammonia is also performed without the necessity of isolating hazardous[23] **49**.



Conclusions

Allenyl azides turn out to be short-lived intermediates as has been shown by the present study. Therefore, all attempts to isolate these species[3–5] (at room temperature) are expected to be unsuccessful. Triazoles have not been recognized as subsequent products of allenyl azides[3] or have been taken for the latter[5]. Since propargyl azides are readily converted to allenyl azides by thermal rearrangement, transformation to triazoles via triazafulvenes presents a novel one-pot procedure for the preparation of *N*-unsubstituted 1,2,3-triazoles which may be a valuable addition to other synthetic methods[12,13,41,42]. The new advantageous way to 1,2,3-triazoles utilizes sodium azide avoiding expensive or violently explosive reactants.

Thanks are due to Mrs. *E. Reißaus* for experimental assistance.

Experimental

General: Melting points (uncorrected): Büchi 510 apparatus. – Optical rotations: Perkin-Elmer 141 polarimeter, sample cells kept at constant temp. by a thermostat[43]. – Elemental analyses: Firma Beller, Göttingen. – Further instrumentation has been described in ref.[1,44].

Warning: All propargyl azides[23,44,45] are known to be potentially explosive. These compounds should be handled only in small quantities or in solution, e. g. using the one-pot procedure to synthesize triazoles. Elemental analyses of azides could not be performed because of unstability and explosive decomposition.

Treatment of 3-Bromo-3-methyl-1-butyne (**1**) *or 1-Iodo-3-methyl-1,2-butadien* (**3**) *with Sodium Azide:* Using a mixture of 30 mg (0.20 mmol) of **1**[6,7] in 400 µl of [D_6]ethanol and 13 mg (0.20 mmol) of sodium azide in 100 µl of D_2O, the experiment described by Shiner and Humphrey[5] was repeated in an NMR tube (20–30°C). The chemical shifts and the changes of the reported ^{1}H-NMR signals were confirmed, but the assignments of structures had to be corrected in part. At first, the exchange of the acetylenic hydrogen atom of **1** [δ = 1.99 (s, Me), 3.16 (s, HC≡C) compared to TMS as internal standard] for deuterium and the appearence of methyl resonances of **5** (δ = 1.49, s, main product) and **9** (δ = 1.68, s) were observed. After that – when most of the sodium azide had been consumed – the signals of **8** (δ = 2.14, br.) and **10** (δ = 1.61, s) as well as the resonances of the solvolysis products of **1** (**12**, 2-methyl-3-butyn-2-ol, and 2-methyl-1-buten-3-yne[46]) increased. At the same time the decrease of the signals of **1** and **5** was observed. After removal of volatile components (20°C/0.001 Torr) the residue, dissolved in [D_6]ethanol/D_2O, showed only the resonances of **8**–**10**. Assignments of ^{1}H-NMR signals of **5** and **8**–**10** were confirmed by adding the pure compounds to the mixtures obtained from **1** and sodium azide in [D_6]ethanol/D_2O.

A mixture of 3.0 g (20 mmol) of **1** in 40 ml of ethanol and 1.3 g (20 mmol) of sodium azide in 10 ml of water was stirred for 60 h at room temp. After removal of volatile components (40°C/10 Torr) the residue was repeatedly extracted with ether. Drying with $MgSO_4$ and evaporation of the solvent gave 1.59 g of a slightly yellow oil. NMR spectra (^{1}H and ^{13}C) showed the resonances of **9** and **10** (main products) as well as the signals of **8**.

The reaction of **1** with sodium azide in [D_4]methanol/D_2O (2:1) was performed in an NMR tube as described for the treatment of **1** with sodium azide in [D_6]ethanol/D_2O. ^{1}H-NMR signals of the methyl groups of **5** (δ = 1.47, s), **9** (δ = 1.66, s), **11** (δ = 1.58, s), **8** (δ = 2.07, br.), **13** (δ = 1.43, s), 2-methyl-3-butyn-2-ol (δ = 1.46, s), and 2-methyl-1-buten-3-yne (δ = 1.85, t) as well as the analogous changes in the intensity of the signals were observed. Assignments of all NMR resonances were confirmed by adding authentic samples to the reaction mixtures.

To a solution of 1.3 g (20 mmol) of sodium azide in 17 ml of water was added 1.33 g (9.05 mmol) of **1** and 33 ml of methanol. After stirring at room temp. for 20 h, volatile components were removed at 70°C/10 Torr. The residue was carefully recondensed

at 0.001 Torr to give 430 mg of a colourless oil which consisted of equal parts of **9** (16% yield) and **11** (16% yield) as shown by NMR spectra (^1H and ^{13}C). The two products were separated by microdistillation at 0.001 Torr. Isolation by preparative GC was accompanied by partial decomposition of **9**.

Treatment of **3** with sodium azide in [D_4]methanol/D_2O was performed in an NMR tube as described for the reaction of **1**. ^1H-NMR spectra indicated signals of **5** (and other solvolysis products) as well as **8**, **9**, and **11**. Compared to **1** the solubility and the reactivity of **3** was low.

4-(1-Azido-1-methylethyl)-1H-1,2,3-triazole (**9**): A solution of **1** (1.33 g, 9.0 mmol) and sodium azide (1.3 g, 20 mmol) in acetone (40 ml) and water (40 ml) was stirred for 6 d at room temp. After removal of volatile components at 10 Torr, the residue was repeatedly extracted with ether. Drying with $MgSO_4$ and evaporation of the solvent yielded 590 mg (43%) of crude **9** which was purified by microdistillation at 0.001 Torr to give a colourless oil. – IR (CCl_4): ν = 2110 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 1.71 (s, 6H), 7.71 (s, 1H), 10.4 (br. s, 1H, position concentration-dependent). – ^{13}C NMR ($CDCl_3$): δ = 27.1 (q, J = 129 Hz), 58.6 (s), 127.6 (d, $J \approx$ 189 Hz), 150.8 (s). – ^{15}N NMR[8] [D_2O/pyridine (1:1), $MeNO_2$ as external standard]: δ = −284.6 (N_α), −161.5 (N_γ), −135.8 (N_β), −93.4, −79.2, −60.4. – GC-MS[47] (70 eV): *m/z* (%) = 110 (100) [$M^+ - N_3$], 109 (18), 82 (9), 68 (11), 55 (18).

Isolation and Reactions of 3-Azido-3-methyl-1-butyne (**5**): At room temp. **3**[7,10] (431 mg, 2.22 mmol) was added dropwise to a supercooled melt of hexadecyltributylphosphonium azide (QN_3)[11] (1.14 g, 2.43 mmol) and ether (0.3 ml). The mixture was stirred for 1.5 h and recondensed at 0.001 Torr giving **5** (44% yield) and **3** (14% recovered) in ether. **5** was isolated by preparative GC (3-m PPG column at 30°C, retention time: 17 min) to yield a colourless liquid. – IR (CCl_4): ν = 3310 cm^{-1}, 2995, 2120, 2080, 1280, 1150. – ^1H NMR ($CDCl_3$): δ = 1.51 (s, 6H), 2.55 (s, 1H). – ^{13}C NMR ($CDCl_3$, −40°C): δ = 28.6 (qq, J = 130, 4 Hz), 56.0 (s), 72.6 (d, J = 253 Hz), 83.3 (dsept, J = 49, 5 Hz). – GC-MS (70 eV): *m/z* (%) = 109 (100) [M^+], 94 (5) [$M^+ - Me$], 81 (43) [$M^+ - N_2$], 80 (32), 67 (12), 66 (12), 54 (58), 53 (51).

When undiluted **5** was allowed to warm to room temp. the clear sample became turbid and formed a white solid of **8** within a few seconds. Diluted in chloroform, half of **5** was transformed to **8** after 16 h at room temp. **8** showed no absorptions for 1-alkynes or azides in the IR spectra, was not volatile, and could not be sublimed at 0.001 Torr. – IR ($CDCl_3$): ν = 3010 cm^{-1}, 1200, 1040. – ^1H NMR ($CDCl_3$): δ = 2.06 (br. s, 6H), 7.3–7.8 (m, 1H).

If **5** was treated with sodium azide in [D_6]ethanol/D_2O, the signals of **8**–**10** were observed in the ^1H-NMR spectra indicating that **8**–**10** were the only succeeding products of **5**. Treatment of **5** with ^{15}N-labelled sodium azide (enrichment 95% for all three nitrogen atoms; Alfred Hempel GmbH & Co. KG, Düsseldorf) in aqueous methanol afforded **9** [IR ($CDCl_3$): ν = 2040 cm^{-1}] and **11**. The label was found only in the azido group of **9** but not in the triazole part of **9** or **11**, as shown by ^{15}N-NMR spectroscopy[8]. Using ^{15}N-labelled sodium azide (enrichment 49% for the terminal nitrogen atoms; Ergotron AG, Switzerland) only two ^{15}N-NMR signals of **9** were observed permitting unequivocal assignments of N_α, N_β, and N_γ. If **1** was treated with ^{15}N-labelled sodium azide in aqueous methanol in a control experiment, ^{15}N-NMR spectra showed signals for azido group *and* triazole part of **9** and **11**. The reaction of **5** with aqueous methanol gave only **11**. Using [D_4]methanol/D_2O the rate of this transformation, which agreed with the rate of the conversion **5** → **11** starting with **1** and sodium azide, could be estimated.

A solution of 220 mg (0.93 mmol) of **6**[4] and 1.30 g (23.2 mmol) of potassium hydroxide in 6 ml of methanol was allowed to stand at room temp. in the dark for 19 d. The solvent was removed at 10 Torr, ice/water was added to the residue, and the mixture was extracted three times with ether. After drying with $MgSO_4$, the solvent was evaporated at 10 Torr to give 100 mg of a residue consisting of **11** (45% yield) and **6** (19% recovered) as shown by ^1H-NMR and ^{13}C-NMR spectra.

4-(1-Ethoxy-1-methylethyl)-1H-1,2,3-triazole (**10**) *from* **12**: In a pressure vessel 14.3 g (128 mmol) of **12**[14] and 18.4 g (160 mmol) of trimethylsilyl azide were heated at 114°C for 5 d. After distillation at 0.01 Torr the fraction boiling at 37–38°C was added dropwise to 100 ml of ethanol. Volatile components were removed at 10 Torr to yield 10.6 g (54%) of **10**. The colourless oil was purified by microdistillation (50–60°C/0.001 Torr) to give a waxy solid (m. p. ca. 40°C). Attempts to distill **10** at higher temp. led to partial decomposition of the material by elimination of ethanol. – IR (CCl_4): ν = 3450 cm^{-1}, 3160 (br.), 2790, 2920, 1160, 1100, 1060. – ^1H NMR ($CDCl_3$): δ = 1.12 (t, J = 7 Hz, 3H), 1.63 (s, 6H), 3.31 (q, J = 7 Hz, 2H), 7.70 (s, 1H), 12.8 (br. s, 1H, position concentration-dependent). – ^{13}C NMR ($CDCl_3$): δ = 15.7 (q), 27.2 (q), 58.5 (t), 72.4 (s), 129.2 (d), 151.1 (s). – MS[47] (70 eV): *m/z* (%) = 156 (0.4) [$M^+ + 1$], 140 (77) [$M^+ - Me$], 112 (100) [$M^+ - HN_3$], 110 (90) [$M^+ - OEt$].

$C_7H_{13}N_3O$ (155.2) Calcd. C 54.17 H 8.44 N 27.07
Found C 54.23 H 8.34 N 27.10

4-(1-Methoxy-1-methylethyl)-1H-1,2,3-triazole (**11**) *from* **13**: In a pressure vessel 6.0 g (61 mmol) of **13**[15] and 8.8 g (76 mmol) of trimethylsilyl azide were heated at 114°C for 85 h. The mixture was recondensed at 0.001 Torr and added dropwise to 100 ml of ethanol. Volatile components were removed at 10 Torr to yield 3.4 g (39%) of **11** as an oil which solidified to colourless crystals, m. p. 75°C (from petroleum ether). If **13** was treated with trimethylsilyl azide at 150°C, the yield of **11** decreased drastically. In this case triazoles resulting from elimination of methanol became main products. – IR (CCl_4): ν = 3460 cm^{-1}, 3180 (br.), 2990, 1180, 1080. – ^1H NMR ($CDCl_3$): δ = 1.63 (s, 6H), 3.15 (s, 3H), 7.69 (s, 1H), 13.4 (br. s, 1H, position concentration-dependent). – ^{13}C NMR ($CDCl_3$): δ = 26.5 (q, J = 127 Hz), 50.6 (q, J = 141 Hz), 72.8 (s), 129.0 (d, $J \approx$ 193 Hz), 150.2 (s). – ^{15}N NMR[8] [D_2O/pyridine (1:1), $MeNO_2$ as external standard]: δ = −87.0, −75.3, −71.5. – GC-MS (70 eV): *m/z* (%) = 126 (100) [$M^+ - Me$], 110 (37) [$M^+ - OMe$], 94 (52).

$C_6H_{11}N_3O$ (141.2) Calcd. C 51.05 H 7.85 N 29.77
Found C 50.94 H 7.71 N 29.88

4-(1-Methoxyethyl)-1H-1,2,3-triazole (**23**) *from* **20**: The tosylate **20**[21] (10 g, 45 mmol) was added to a solution of lithium azide (7.6 g, 155 mmol) in methanol (40 ml) and stirred vigorously at 40°C for 30 min. After recondensing in vacuo (0.01 Torr) the distillate was diluted with methanol (450 ml) and stirred at 20–40°C for 4 d. Distillation afforded 4.66 g (82%) of **23** as a colourless liquid, b. p. 60°C/0.001 Torr. Treatment of **20** with sodium azide gave also **23**, but due to the low solubility the volume of methanol had to be enlarged. – IR (CCl_4): ν = 3460 cm^{-1}, 3180 (br.), 2990, 2940, 1120, 1095. – ^1H NMR ($CDCl_3$): δ = 1.57 (d, J = 6.7 Hz, 3H), 3.34 (s, 3H), 4.68 (q, J = 6.7 Hz, 1H), 7.72 (s, 1H), 14.3 (br. s, 1H, position concentration-dependent). – ^{13}C NMR ($CDCl_3$): δ = 20.7 (q), 55.9 (q), 71.1 (d), 127.9 (d), 147.6 (s). – MS (70 eV): *m/z* (%) = 126 (1) [$M^+ - 1$], 112 (100) [$M^+ - Me$], 97 (23), 96 (26) [$M^+ - OMe$].

$C_5H_9N_3O$ (127.2) Calcd. C 47.23 H 7.13 N 33.05
Found C 47.33 H 7.01 N 33.04

p-Toluenesulfonyl chloride (3.82 g, 20.0 mmol) was added slowly to a solution of *S*-(−)-**19**[25] (700 mg, 10 mmol, 83% ee) in dioxane (7 ml) and pyridine (5 ml) which was stirred at 0°C. After stirring at room temp. for 19 h, the mixture was cooled to 0°C to add 1 ml of water within 20 min. The mixture was diluted with 50 ml of ice/water, stirred at 0°C for 1 h, and extracted twice with ether. The combined organic layers were washed with dilute sulfuric acid (twice) and aqueous $NaHCO_3$ and dried with $MgSO_4$. The solvent was removed in vacuo to yield 1.5 g (67%) of pure (^{1}H NMR) *S*-**20** which was treated with lithium azide in methanol, as described for racemic **20**. **23** from *S*-**20** showed no optical activity: $|[\alpha]_D^{25}| \leq 0.017$ (c = 17.2 in $CHCl_3$). Consequently, the conversion *S*-**20** → **23** was accompanied with 99.97% racemization.

Isolation and Reactions of 3-Azido-1-butyne (**21**): 1.0 g (4.5 mmol) of **20** was added slowly to a supercooled melt of QN_3[11] (2.1 g, 4.5 mmol, 45°C). The mixture was stirred at 50°C for 10 min and recondensed at 0.001 Torr to give **21** (350 mg, 83%) as a colourless liquid which could be purified by preparative GC (3-m PPG column at 30°C, retention time: 20 min). – IR (CCl_4): ν = 3310 cm^{-1}, 2990, 2920, 2850, 2130, 2100, 1235. – ^{1}H NMR ($CDCl_3$): δ = 1.46 (d, J = 7.1 Hz, 3H), 2.55 (d, J = 2.2 Hz, 1H), 4.18 (qd, J = 7.1, ca. 2 Hz, 1H). – ^{13}C NMR ($CDCl_3$): δ = 21.2 (qd, J = 130, 4 Hz), 48.1 (d, J = 149 Hz), 73.9 (dd, J = 252, 4 Hz), 80.4 (d, J = 50 Hz). – GC-MS (70 eV): *m/z* (%) = 95 (17) [M^+], 80 (3) [M^+ – Me], 66 (5), 53 (100) [M^+ – N_3].

A solution of **21** in methanol was stirred at 20–40°C for 4 d. The solvent was evaporated to yield **23** as sole product (identification by ^{1}H-NMR and ^{13}C-NMR spectra). If **21** in chloroform was kept at 60°C for 4.5 h, most of the starting material was converted to a new compound which could not be recondensed at 0.001 Torr. This polymeric material showed only broad NMR signals[22].

20 (1.5 g, 6.7 mmol; or *S*-**20**) was added to a solution of lithium azide (1.14 g, 23 mmol) in methanol (6 ml) and stirred vigorously at 40°C for 30 min. After recondensing in vacuo (0.01 Torr) the distillate was hydrogenated using hydrogen (1 bar, room temp., 1 d) and PtO_2. The mixture was filtered, added to 10 ml of dilute HCl, and evaporated at 10 Torr. The residue was dissolved in 700 µl of water and added to an excess of solid potassium hydroxide. The organic layer was separated, and the aqueous layer was extracted with pentane. After repeated drying of the combined organic layers using potassium hydroxide, **24** was isolated by preparative GC (1-m Carbowax + KOH column at 30°C, retention time: 1 min, yield 153 mg, 31%) and identified by comparison (^{1}H NMR) with an authentic sample.

4-(1-Methoxyethyl)-1H-1,2,3-triazole (**23**) *from* **22**: In a pressure vessel **22**[24] (8.0 g, 95 mmol) and trimethylsilyl azide (13.7 g, 119 mmol) were heated at 114°C for 6 d. The mixture was recondensed at 0.001 Torr and added dropwise to 100 ml of ethanol. Volatile components were removed at 30°C/0.001 Torr to yield 7.6 g (63%) of **23** identical with **23** from **20** as shown by ^{1}H-NMR and ^{13}C-NMR spectra. If *S*-(−)-**19** was transformed[24] to *S*-**22** and subsequently treated with trimethylsilyl azide as described for racemic **22**, the resulting *S*-(−)-**23** (after distillation) showed a high rotation value: $[\alpha]_D^{25}$ = −62.63 (c = 20 in $CHCl_3$). ^{1}H-NMR spectroscopy using tris[3-(trifluoromethylhydroxymethylene)-d-camphorato]europium [Eu(tfc)$_3$] indicated 82% ee giving $[\alpha]_D^{25}$ (max.) = −76 (c = 20 in $CHCl_3$).

4-Azido-2-butyn-1-ol (**36**): Sodium azide (50 g, 0.77 mol) in water (250 ml) and **35**[34] (25 g, 0.24 mol) in ethanol (250 ml) were stirred at 50°C for 1 h. The mixture was added to ice/water and extracted repeatedly with ether. The combined organic layers were washed with water and dried with $MgSO_4$. The solvent was evaporated (20°C/10 Torr) to yield 19.3 g (73%) of **36** as a colourless liquid which could be purified by recondensation at ca. 40°C/0.001 Torr. – IR (CCl_4): ν = 3610 cm^{-1}, 3320 (br.), 2920, 2140, 2090, 1380, 1340, 1265, 1250, 1135, 1020. – ^{1}H NMR ($CDCl_3$): δ = 2.7 (br. s, 1H, position concentration-dependent), 3.95 (br. s, 2H), 4.32 (t, J = 2 Hz, 2H). – ^{13}C NMR ($CDCl_3$): δ = 39.9 (t, J = 149 Hz), 50.4 (t, J = 148 Hz), 77.5 (s), 85.4 (s).

5-(Methoxymethyl)-1H-1,2,3-triazole-4-methanol (**37**): 1.17 g (10.5 mmol) of **36** and 20 ml of methanol were stirred at 60°C for 20 h. After removal of the solvent at 10 Torr the residue was recondensed at 100–120°C/0.001 Torr to give 970 mg (64%) of **37** as a light-yellow oil which could be purified by microdistillation. – IR ($CDCl_3$): ν = 3440 cm^{-1}, 3200 (br.), 2940, 1100, 1030, 895. – ^{1}H NMR (D_2O): δ = 3.08 (s, 3H), 4.33 (s, 2H), 4.47 (s, 2H). – ^{13}C NMR (D_2O, TMS as external standard): δ = 53.1 (t, J = 145 Hz), 57.7 (qt, J = 143, 4 Hz), 63.1 (tq, J = 146, 5 Hz), 138.7 (s), 141.4 (s). – MS (70 eV): *m/z* (%) = 142 (5) [M^+ – 1], 125 (82) [M^+ – H_2O], 111 (100) [M^+ – MeOH], 95 (96).

$C_5H_9N_3O_2$ (143.2) Calcd. C 41.95 H 6.34 N 29.35
Found C 41.87 H 6.27 N 29.38

4,5-Bis(methoxymethyl)-1H-1,2,3-triazole (**41**) *from* **38** *or* **39**: Sodium azide (3.67 g, 56.5 mmol) in water (15 ml), **38**[35] (14.68 g, 61.1 mmol), and methanol (61 ml) were stirred at room temp. for 24 h. The mixture was diluted with 600 ml of methanol and refluxed for 6 h. After removal of the solvent at 10 Torr the residue was treated with ether in a Soxhlet apparatus. The extract was dried with $MgSO_4$ and concentrated in vacuo to afford 7.81 g (88%) of **41** which could be purified by microdistillation at 0.001 Torr (b. p. ca. 120°C) to yield a colourless waxy solid (m. p. below 30°C). Starting with **39**[36], an analogous synthesis of **41** could be performed (yield 62%), but nucleophilic substitution of **39** was slower. – IR (CCl_4): ν = 3450 cm^{-1}, 3180 (br.), 2920, 1100. – ^{1}H NMR ($CDCl_3$): δ = 3.36 (s, 6H), 4.62 (s, 4H), 12.0 (br. s, 1H, position concentration-dependent). – ^{13}C NMR ($CDCl_3$): δ = 58.1 (q), 64.6 (t), 141.3 (s). – MS (70 eV): *m/z* (%) = 157 (2) [M^+], 127 (10), 126 (8) [M^+ – OMe], 125 (100) [M^+ – MeOH], 96 (78) [M^+ – OMe – MeOH], 95 (55) [M^+ – 2 MeOH], 69 (17).

$C_6H_{11}N_3O_2$ (157.2) Calcd. C 45.85 H 7.05
Found C 46.09 H 6.92

If **38** was treated with sodium azide in methanol/water as described and the time of reflux (after dilution with methanol) was shortened to 3 h or fewer, 1-azido-4-methoxy-2-butyne (**40**) could be isolated as a colourless liquid. – IR (CCl_4): ν = 2130 cm^{-1}, 1125, 1100. – ^{1}H NMR ($CDCl_3$): δ = 3.39 (s, 3H), 3.96 (br. s, 2H), 4.16 (t, J = 2 Hz, 2H).

4,5-Bis(methoxymethyl)-1H-1,2,3-triazole (**41**) *from* **42**: In a pressure vessel **42**[37] (8.0 g, 70 mmol) and trimethylsilyl azide (16.0 g, 139 mmol) were heated at 114°C for 10 d. After removal of the excess of azide at 10 Torr the residue was distilled at 0.001 Torr (b. p. 63–120°C). The complete distillate was added dropwise to 100 ml of methanol. After evaporation of the solvent, distillation at 0.001 Torr gave 8.84 g (80%) of **41**, identical with **41** from **38** or **39** as shown by IR and ^{1}H-NMR spectra.

4-(Methoxymethyl)-5-phenyl-1H-1,2,3-triazole (**44**): Sodium azide (1.17 g, 18 mmol) in water (5 ml), **43**[38] (5.72 g, 20 mmol), and methanol (15 ml) were stirred vigorously at 35°C for 2.5 h. After this time the complete consumption of sodium azide could be confirmed by measurement of pH which decreased to 5–6. The mixture was added to 50 ml of methanol and refluxed for 45 h. The solution was made strongly alkaline by addition of solid sodium hydroxide (3.33 g), evaporated at 10 Torr, diluted with water, and washed

twice ether. The aqueous layer was adjusted to pH = 5–6 with dilute HCl and extracted continuously with ether for 1 d. After drying with $MgSO_4$, the solvent was removed in vacuo to afford **44** (2.48 g, 73%) as a light-yellow solid, m. p. 145°C (from ethyl acetate). – IR ($CDCl_3$): ν = 3440 cm^{-1} (NH), 3170 (NH), 2930, 1090. – ^1H NMR ($CDCl_3$): δ = 3.45 (s, 3H), 4.71 (s, 2H), 7.38 (br. t, $J \approx 7$ Hz, 1H), 7.44 (br. t, $J \approx 7$ Hz, 2H), 7.77 (br. d, $J \approx 7$ Hz, 2H), 13.1 (br. s, 1H, position concentration-dependent). – ^{13}C NMR ($CDCl_3$): δ = 58.1 (q), 64.8 (t), 127.6 (d), 128.6 (d), 128.8 (d), 129.6 (s), 139.5 (s), 144.6 (s). – MS (70 eV): *m/z* (%) = 189 (98) [M^+], 174 (55) [M^+ – Me], 159 (86), 129 (63), 103 (100).

$C_{10}H_{11}N_3O$ (189.2) Calcd. C 63.48 H 5.86 N 22.21
Found C 63.50 H 5.85 N 22.27

4-(Methoxyphenylmethyl)-1H-1,2,3-triazole (**46**): Sodium azide (327 mg, 5.03 mmol) in water (1.4 ml), **45**[39] (1.07 g, 5.5 mmol), and methanol (5 ml) were stirred vigorously at 20°C (external cooling). When pH had decreased to 6–7 (ca. 30 min), the mixture was added to 30 ml of methanol and refluxed for 19 h. The solution was made strongly alkaline by addition of solid sodium hydroxide (2.0 g), evaporated at 10 Torr, diluted with water, and washed with ether. The aqueous layer was adjusted to pH = 5–6 with dilute HCl, evaporated at 70°C/10 Torr, and extracted repeatedly with ether. After drying with $MgSO_4$, the solvent was removed in vacuo (room temp./0.001 Torr) to yield 830 mg (87%) of **46**. The product could be purified by CC (silica gel, eluent: ether) or careful microdistillation at 0.001 Torr to give a colourless oil. – IR (CCl_4): ν = 3450 cm^{-1}, 3160 (br.), 2920, 1450, 1095. – ^1H NMR ($CDCl_3$): δ = 3.40 (s, 3H), 5.53 (s, 1H), 7.3–7.5 (m, 5H), 7.54 (s, 1H), 14.2 (br. s, 1H, position concentration-dependent). – ^{13}C NMR ($CDCl_3$): δ = 57.0 (q), 78.1 (d), 127.0 (d), 128.2 (d), 128.6 (d), 130.1 (d), 139.6 (s), 148.1 (s). – MS (70 eV): *m/z* (%) = 189 (31) [M^+], 174 (33) [M^+ – Me], 159 (32), 158 (100) [M^+ – OMe], 96 (51), 77 (64) [Ph^+].

$C_{10}H_{11}N_3O$ (189.2) Calcd. C 63.48 H 5.86 N 22.21
Found C 63.44 H 5.75 N 21.94

4-⟨[(1-Methylethyl)thio]methyl⟩-1H-1,2,3-triazole (**50**) *from* (**47**): Sodium azide (3.25 g, 50 mmol) in 45 ml of water and **47** (6.64 g, 4.2 ml, 56 mmol) in 90 ml of dioxane were stirred at room temp. for 1 d. After adding 2-propanethiol (22 g, 290 mmol) the mixture was heated at 70°C for 3 h. The solution was saturated with sodium chloride, the organic layer was separated, and the aqueous layer was extracted 4 times with ether. After drying the combined organic layers with $MgSO_4$, distillation afforded **50** (2.46 g, 31%) as a yellow oil, b. p. 105°C/0.01 Torr. – IR (CCl_4): ν = 3460 cm^{-1}, 3170 (br.), 2960, 2920, 2870, 1460, 1150. – ^1H NMR ($CDCl_3$): δ = 1.28 (d, J = 6.8 Hz, 6H), 2.89 (sept, J = 6.8 Hz, 1H), 3.88 (s, 2H), 7.70 (s, 1H), 9.2 (br. s, 1H, position concentration-dependent). – ^{13}C NMR ($CDCl_3$): δ = 22.9 (q), 24.4 (t), 34.8 (d), 130.1 (d), 144.5 (s). – MS (70 eV): *m/z* (%) = 157 (5) [M^+], 142 (2) [M^+ – Me], 115 (4) [M^+ – N_3], 83 (100).

$C_6H_{11}N_3S$ (157.2) Calcd. C 45.83 H 7.05 N 26.72
Found C 45.91 H 6.81 N 26.77

4-⟨[(1-Methylethyl)thio]methyl⟩-1H-1,2,3-triazole (**50**) *from* **52**: In a pressure vessel **52**[40] (9.3 g, 82 mmol) and trimethylsilyl azide (20.3 g, 176 mmol) were heated at 92°C for 3 d and at 114°C for 7 d. After removal of the excess of azide at 10 Torr the residue was distilled at 0.005 Torr. The fraction boiling at 67–71°C (14.46 g) was added dropwise to 200 ml of methanol. After evaporation of the solvent, distillation at 0.01 Torr gave 9.81 g (76%) of **50**, identical with **50** from **47** as shown by NMR spectra.

1H-1,2,3-Triazole-4-methylamine (**51**): Sodium azide (3.25 g, 50.0 mmol) in 45 ml of water and **48**[21a] (11.7 g, 56 mmol) in 110 ml of dioxane were stirred at room temp. for 36 h. After recondensing in vacuo (room temp./0.001 Torr) the mixture was diluted with 600 ml of concd. aqueous ammonia and stirred at 50–60°C for 3 d. Volatile components were removed at 10 Torr to yield **51** (3.76 g, 77%) as a colourless solid which could be purified by crystallization from water/dioxane or sublimation (140°C/0.01 Torr), m. p. 206°C. Starting with **47**, **51** could be prepared in an analogous way. – IR (KBr): ν = 3300–2000 cm^{-1} (very broad band), 2620, 2180, 1645, 1560, 1260, 1220, 1090, 1045, 975, 835, 665. – ^1H NMR (D_2O): δ = 4.05 (s, 2H), 7.57 (s, 1H). – ^{13}C NMR (D_2O, TMS as external standard): δ = 34.6 (t), 130.0 (d), 139.6 (s). – MS (70 eV): *m/z* (%) = 98 (39) [M^+], 97 (100), 82 (10) [M^+ – NH_2], 70 (46) [M^+ – N_2], 55 (16) [M^+ – HN_3].

$C_3H_6N_4$ (98.11) Calcd. C 36.73 H 6.16 N 57.11
Found C 36.71 H 6.34 N 57.24

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[1] Part 5: K. Banert, *Chem. Ber.* **122** (1989) 123.
[2] G. Smolinsky, C. A. Pryde in *The Chemistry of the Azido Group* (S. Patai, Ed.), p. 555, Wiley-Interscience, London 1971; G. L'abbé, A. Hassner, *Angew. Chem.* **83** (1971) 103; *Angew. Chem. Int. Ed. Engl.* **10** (1971) 98; A. Hassner in *Azides and Nitrenes* (E. F. V. Scriven, Ed.), p. 35, Academic Press, Orlando, FL (USA) 1984.
[3] G. L'abbé, M. Mahy, M. Bollyn, G. Germain, G. Scheefer, *Bull. Soc. Chim. Belg.* **92** (1983) 881; G. L'abbé, *ibid.* **93** (1984) 579.
[4] A. Hassner, J. Keogh, *J. Org. Chem.* **51** (1986) 2767.
[5] V. J. Shiner, Jr., J. S. Humphrey, Jr., *J. Am. Chem. Soc.* **89** (1967) 622.
[6] V. J. Shiner, Jr., J. W. Wilson, *J. Am. Chem. Soc.* **84** (1962) 2402; L. Brandsma, H. D. Verkruijsse, *Synthesis of Acetylenes, Allenes, and Cumulenes*, p. 219, Elsevier, Amsterdam 1981.
[7] T. L. Jacobs, W. L. Petty, *J. Org. Chem.* **28** (1963) 1360.
[8] The emphasized protons in **9**–**11**, **17**, **23**, **28**, **37**, **41**, **44**, **46**, **50**, and **51** may be bound to each nitrogen atom of the heterocycles. This tautomerism[9] causes significant broadening of signals as well as concentration-dependent and solvent-dependent chemical shifts in ^{13}C-NMR and ^{15}N-NMR spectroscopy (9.4 Tesla, 30°C).
[9] M. Begtrup, *J. Chem. Soc., Perkin Trans. 2*, **1976**, 736; S. Toppet, G. Wouters, G. Smets, *Org. Magn. Reson.* **11** (1978) 578.
[10] P. M. Greaves, M. Kalli, P. D. Landor, S. R. Landor, *J. Chem. Soc. C*, **1971**, 667.
[11] D. Landini, A. Maia, F. Montanari, *J. Am. Chem. Soc.* **100** (1978) 2796; *Nouv. J. Chim.* **3** (1979) 575; D. Landini, A. Maia, F. Montanari, F. Rolla, *J. Org. Chem.* **48** (1983) 3774; K. Banert, W. Kirmse, *J. Am. Chem. Soc.* **104** (1982) 3766; K. Banert, *Chem. Ber.* **118** (1985) 1564.
[12] Aprotic solvents and high temperatures or alkynes with electron-withdrawing groups are required to effect the reaction of acetylenes with sodium azide to triazoles[13].
[13] A. N. Nesmeyanov, M. I. Rybinskaya, *Dokl. Akad. Nauk SSSR* **158** (1964) 408 [*Chem. Abstr.* **61** (1964) 14664g]; F. P. Woerner, H. Reimlinger, *Chem. Ber.* **103** (1970) 1908; Y. Tanaka, S. R. Velen, S. I. Miller, *Tetrahedron* **29** (1973) 3271, and references cited therein; T. L. Gilchrist, G. E. Gymer, *Adv. Heterocycl.*

Chem. **16** (1974) 33; E. J. Trybulski, L. Benjamin, S. Vitone, A. Walser, R. I. Fryer, *J. Med. Chem.* **26** (1983) 367.

[14] S. S. Sabirov, S. S. Shukurov, M. P. Mukhamedkulova, T. I. Sverchkova, *J. Org. Chem. USSR (Engl. Transl.)* **15** (1979) 812.

[15] E. J. Corey, D. Floyd, B. H. Lipshutz, *J. Org. Chem.* **43** (1978) 3418.

[16] These types of reactions were investigated by L. Birkofer, P. Wegner, *Chem. Ber.* **99** (1966) 2512; L. Birkofer, A. Ritter, P. Richter, *ibid.* **96** (1963) 2750; L. Birkofer, A. Ritter, H. Uhlenbrauck, *ibid.* **96** (1963) 3280; L. Birkofer, A. Ritter, *Angew. Chem.* **77** (1965) 414; *Angew. Chem. Int. Ed. Engl.* **4** (1965) 417.

[17] For analogous triazolines from allylic azides see: A. Gagneux, S. Winstein, W. G. Young, *J. Am. Chem. Soc.* **82** (1960) 5956.

[18] A similar tetrazole is postulated: G. Smolinsky, C. A. Pryde, *J. Org. Chem.* **33** (1968) 2411.

[19] For the analogous rearrangement of allylic azides see: C. A. van der Werf, V. L. Heasley, *J. Org. Chem.* **31** (1966) 3534.

[20] For the reaction of triazafulvenes with methanol see: E. M. Burgess, J. P. Sanchez, *J. Org. Chem.* **38** (1973) 176; **39** (1974) 940.

[21] [21a] W. Reppe and co-workers, *Liebigs Ann. Chem.* **596** (1955) 1. – [21b] H. Heimgartner, J. Zsindely, H.-J. Hansen, H. Schmid, *Helv. Chim. Acta* **55** (1972) 1113. – [21c] A. Wunderli, T. Winkler, H.-J. Hansen, *ibid.* **60** (1977) 2436.

[22] ^{1}H-NMR and ^{13}C-NMR spectra of the polymer from **21** are compatible with structures of 1,4- and 1,5-disubstituted triazoles; for comparison see ref.[23] and H. Priebe, to be published.

[23] M. G. Baldwin, K. E. Johnson, J. A. Lovinger, C. O. Parker, *J. Polymer Sci, Part B,* **5** (1967) 803.

[24] W. Kirmse, A. Engelmann, J. Heese, *Chem. Ber.* **106** (1973) 3073.

[25] J.-P. Vigneron, V. Bloy, *Tetrahedron Lett.* **1979**, 2683.

[26] P. Bruck, I. N. Denton, A. H. Lamberton, *J. Chem. Soc.* **1956**, 921.

[27] See also K. E. Johnson, J. A. Lovinger, C. O. Parker, M. G. Baldwin, *J. Polymer Sci., Part B,* **4** (1966) 977.

[28] The rate of the rearrangement of allylic azides is increased by additional methyl groups, see ref.[17] and K. Banert, unpublished results.

[29] L. A. Burke, G. Leroy, M. T. Nguyen, M. Sana, *J. Am. Chem. Soc.* **100** (1978) 3668; see also T. Yamabe, M. Kaminoyama, T. Minato, K. Hori, K. Isomura, H. Taniguchi, *Tetrahedron* **40** (1984) 2095.

[30] G. Smolinsky, *J. Am. Chem. Soc.* **83** (1961) 4483; *J. Org. Chem.* **27** (1962) 3557; A. Hassner, F. W. Fowler, *J. Am. Chem. Soc.* **90** (1968) 2869; G. L'abbé, G. Mathys, *J. Org. Chem.* **39** (1974) 1778; G. L'abbé, *Angew. Chem.* **87** (1975) 831; *Angew. Chem. Int. Ed. Engl.* **14** (1975) 775; *New Synthetic Methods* **5** (1979) 1; A. Hassner, N. H. Wiegand, H. E. Gottlieb, *J. Org. Chem.* **51** (1986) 3176.

[31] M. Henriet, M. Houtekie, B. Techy, R. Touillaux, L. Ghosez, *Tetrahedron Lett.* **21** (1980) 223; C. Bernard, L. Ghosez, *J. Chem. Soc., Chem. Commun.* **1980**, 940; R. Carrié, D. Danion, E. Ackermann, R. W. Saalfrank, *Angew. Chem.* **94** (1982) 294; *Angew. Chem. Int. Ed. Engl.* **21** (1982) 288; R. W. Saalfrank, E. Ackermann, M. Fischer, U. Wirth, *Chem. Ber.* **120** (1987) 2003.

[32] R. Huisgen, *Angew. Chem.* **92** (1980) 979; *Angew. Chem. Int. Ed. Engl.* **19** (1980) 947.

[33] J. S. Meek, J. S. Fowler, *J. Am. Chem. Soc.* **89** (1967) 1967; *J. Org. Chem.* **33** (1968) 985; N. S. Zefirov, N. K. Chapovskaya, *J. Org. Chem. USSR (Engl. Transl.)* **4** (1968) 1252.

[34] G. Dupont, R. Dulou, G. Lefebvre, *Bull. Soc. Chim. Fr.* **1954**, 816; R. Stroh, in *Methoden der organischen Chemie* (Houben-Weyl-Müller, Ed.), 4th ed., vol. 5/3, p. 864, Thieme, Stuttgart 1962.

[35] B. Foxman, D. Marten, A. Rosan, S. Raghu, M. Rosenblum, *J. Am. Chem. Soc.* **99** (1977) 2160.

[36] P. P. Montijn, L. Brandsma, J. F. Arens, *Recl. Trav. Chim. Pays-Bas* **86** (1967) 129.

[37] I. Ichikizaki, C.-C. Yao, Y. Fujita, Y. Hasebe, *Bull. Chem. Soc. Jpn.* **28** (1955) 80.

[38] O. A. Prib, I. M. Yasinskii, *J. Org. Chem. USSR (Engl. Transl.)* **4** (1968) 2057.

[39] W. Kirmse, A. Engelmann, *Chem. Ber.* **106** (1973) 3086; J. R. Brooks, D. N. Harcourt, R. D. Waigh, *J. Chem. Soc., Perkin Trans. 1,* **1973**, 2588.

[40] W. E. Truce, D. W. Onken, *J. Org. Chem.* **40** (1975) 3200.

[41] Reviews: W. Lwowski in *1,3-Dipolar Cycloaddition Chemistry* (A. Padwa, Ed.), vol. 1, p. 559, Wiley-Interscience, New York 1984; K. T. Finley, *Triazoles: 1,2,3,* in *The Chemistry of Heterocyclic Compounds* (J. A. Montgomery, Ed.), vol. 39, Wiley, New York 1980.

[42] J. C. Sheehan, C. A. Robinson, *J. Am. Chem. Soc.* **71** (1949) 1436; *ibid.* **73** (1951) 1207; L. W. Hartzel, F. R. Benson, *ibid.* **76** (1954) 667, and references cited therein; T. Fuchigami, T. Goto, M.-Y. Yeh, T. Nonaka, H.-J. Tien, *Bull. Chem. Soc. Jpn.* **57** (1984) 1362; R. T. Chakrasali, H. Ila, H. Junjappa, *Synthesis* **1988**, 453.

[43] Optical rotations were measured in Bochum, Abteilung für Chemie der Ruhr-Universität Bochum.

[44] K. Banert, *Chem. Ber.* **120** (1987) 1891.

[45] H. Priebe, *Angew. Chem.* **96** (1984) 728; *Angew. Chem. Int. Ed. Engl.* **23** (1984) 736; *Acta Chem. Scand., Ser. B,* **38** (1984) 623, 895; K. Banert, *Tetrahedron Lett.* **26** (1985) 5261.

[46] E. D. Bergmann, E. Zimkin, *J. Chem. Soc.* **1950**, 3455.

[47] For mass spectra of *N*-unsubstituted 1,2,3-triazoles see S. I. Miller, R.-R. Lii, Y. Tanaka, *J. Chem. Soc., Perkin Trans. 1,* **1979**, 15.

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