# Reactions of Unsaturated Azides, 12[+]

# Azido-1,2,3-triphenylpropenes of Varying Stabilities: A Corrigendum of Structure Assignment

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*Dedicated to Professor Dieter Hönicke on the occasion of his 60th birthday*

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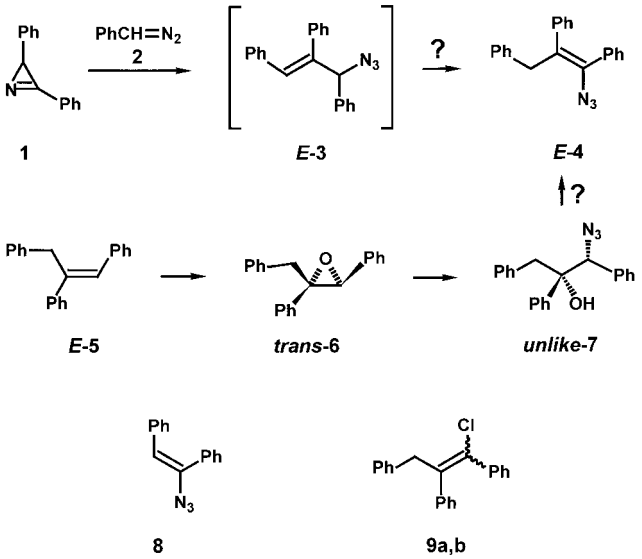
A reinvestigation of the reaction between 2,3-diphenyl-2*H*-azirine (**1**) and phenyldiazomethane (**2**) has shown that a literature report has to be corrected since no vinyl azide **4** but rather the allylic compound 3-azido-1,2,3-triphenyl-1-propene (**3**) is produced. This stable substance, which can also be prepared by substitution reactions of allylic bromide (*E*)-**10** or from alcohol (*E*)-**11**, may be separated into its geometrical isomers (*E*)-**3** and (Z)-**3**, although these equilibrate through rapid [3,3] sigmatropic migration of the azido group. Attempts to synthesize **4** by dehydration of azido alcohols **7** using methanesulfonyl chloride and sulfur dioxide or by elimination of hydrogen chloride from azides **15** led only to **3** and 2-benzyl-2,3-diphenyl-2*H*-azirine (**14**). This heterocycle, which can also be prepared by Neber rearrangement, has been found to be the thermal and photochemical decomposition product of the unstable vinyl azides **4**. However, dehydrations of **7** using thionyl chloride at low temperature have led to the first isolation of 1-azido-1,2,3-triphenyl-1-propenes (**4**). Starting with **3** and various other allylic azides, rearrangement reactions involving sigmatropic shift of the azido group or photochemical *cis–trans* isomerization have been investigated, as have base-catalyzed (prototropic) rearrangements to give vinyl azides.

## Introduction

Vinyl azides have recently been attracting renewed interest, largely because of their manifold reactions.[1][2] The most effective methods for their synthesis[2] include rearrangement reactions, which start from easily accessible allyl or propargyl precursors. Whereas [3,3] sigmatropic isomerizations implying a shift of the azido group into a vinylic position have been thoroughly investigated,[3] rearrangement reactions leading to vinyl azides by migration of a hydrogen atom have scarcely been mentioned.[2d,4]

In a publication by Bowie, Nussey, and Ward,[5] the reaction between the azirine **1** and phenyldiazomethane **2** was reported to give the stable vinyl azide (*E*)-**4** in good yield (Scheme 1). The authors rationalized the formation of this product by postulating the generation of allyl azide (*E*)-**3** as an intermediate that could undergo rapid isomerization via either radical or polar rearrangement pathways to afford (*E*)-**4**. Details of these mechanisms, which would have to have involved a migration of a hydrogen atom, were not given. In order to prove the structure of the surprising product, the authors prepared the oxirane *trans*-**6** from (*E*)-**5** and treated this heterocycle with sodium azide to yield *unlike*-**7**. Dehydration of *unlike*-**7** was claimed to lead to (*E*)-**4**, which was said to be identical to the azide prepared from **1** and **2**.




Scheme 1. Syntheses of vinyl azide (*E*)-**4** published by Bowie, Nussey, and Ward[5]

These results are remarkable for three reasons: First of all, diazo compounds typically react with 2*H*-azirines to give allyl azides.[6] This transformation has been rational-

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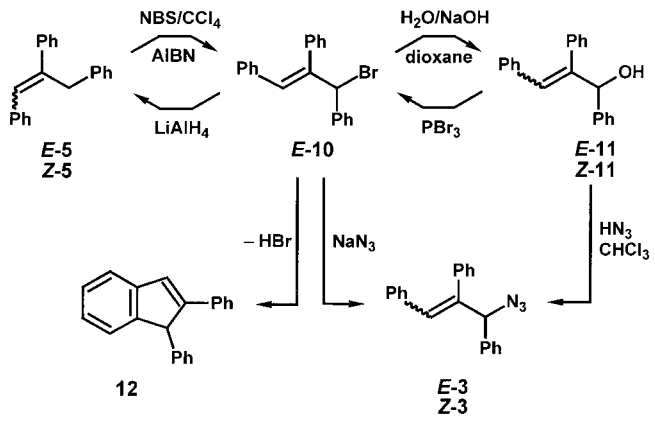
ized in terms of a regioselective 1,3-dipolar cycloaddition to generate a short-lived 1,2,3-triazabicyclo[3.1.0]hex-2-ene, followed by a cycloreversion reaction. To the best of our knowledge, other examples of *vinyl* azides originating from treatment of an azirine with a diazo compound are unknown. Secondly, the azide (*E*)-**4** was reported to be unusually stable in that it was unaffected by boiling toluene.[5] This is in marked contrast to the thermal instability of the vinyl azide **8**, which has been found to undergo loss of nitrogen to afford **1** even below 0°C.[7] The low stability of **8** was explained in terms of the steric hindrance resulting from the *cis* arrangement of the phenyl groups.[8] Thirdly, Bowie, Nussey, and Ward reported that the $^1$H NMR spectrum of (*E*)-**4** featured a singlet at δ = 5.31, which they attributed to the two protons of the methylene group.[5] This chemical shift appeared at unusually low field as compared with the δ values of the analogous benzylic protons of (*E*)-**5** (δ = 4.00),[9] (*Z*)-**5** (δ = 3.65),[9] and **9a,b** (δ = 3.7 and 4.1).[10]

We describe here new and reinvestigated syntheses of the azides **3** and **4**, including a corrigendum of the structure assignment made by Bowie, Nussey, and Ward. Our initial target was the preparation of allyl azide **3** under smooth conditions that would allow study of the rearrangement of **3** to the vinyl isomer **4**.

## Results and Discussion

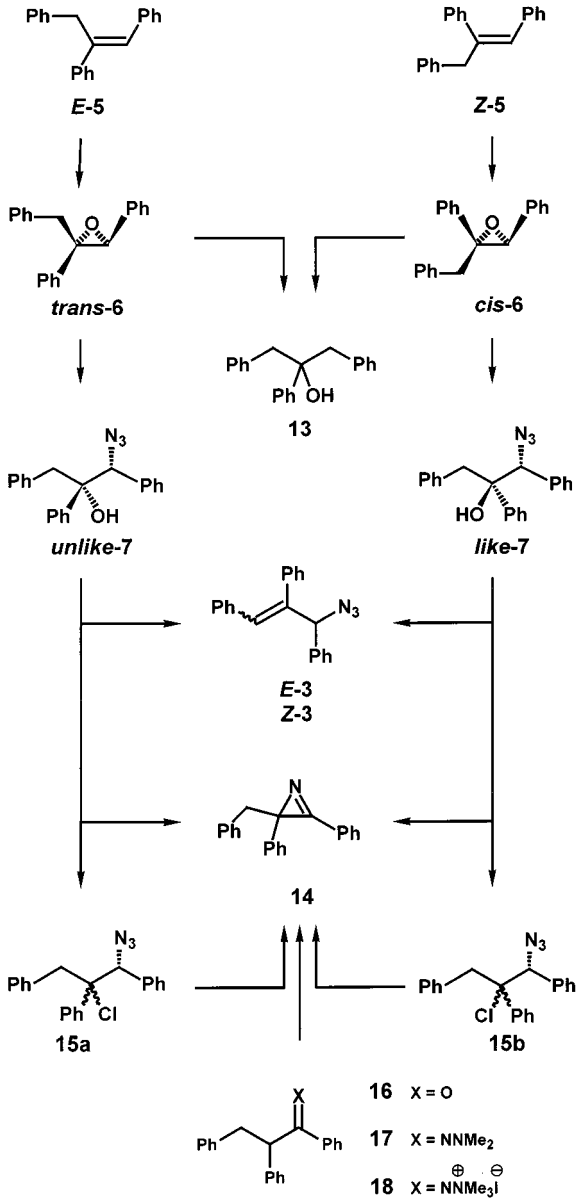
### Synthesis of Azido-1,2,3-triphenylpropenes

Treatment of the hydrocarbon (*E*)-**5**[9][11] with *N*-bromosuccinimide and azodiisobutyronitrile (AIBN) in boiling tetrachloromethane (Scheme 2) leads to the bromide (*E*)-**10** in 72% yield. Alternatively, analogous treatment of (*Z*)-**5**[9][11] or a mixture of both geometrical isomers can also be used to synthesize (*E*)-**10**. The identical product may be prepared almost quantitatively from the alcohol (*E*)-**11**[12][13] and phosphorus tribromide or from (*Z*)-**11**[12][14] and the same reagent in 89% yield. The bromide (*E*)-**10** can be isolated as a colorless solid with m.p. 72°C, but it tends to liberate hydrogen bromide even at room temperature to




Scheme 2. Syntheses of allyl azides **3**

give the indene **12**[13][15] in almost quantitative yield.[16] On treatment with $LiAlH_4$ in diethyl ether, (*E*)-**10** affords **5** in 97% yield with (*E*)/(*Z*) = 5:95. Thus, this stereoselective reaction provides a useful access to (*Z*)-**5**. Hydrolysis of (*E*)-**10** using sodium hydroxide in aqueous dioxane furnishes (*E*)-**11** in 80% yield.




Scheme 3. Syntheses of azido alcohols **7** and the products obtained upon their treatment with methanesulfonyl chloride and sulfur dioxide

Reaction of (*E*)-**10** with sodium azide in aqueous ethanol provides the allyl azide **3** in 78% yield as a colorless solid with m.p. 65°C. On treatment with hydrazoic acid,[17] (*E*)-**11** also produces **3** (25%) and **12** (16%). In both cases, the azide **3** is generated as a mixture with (*E*)-**3**/(*Z*)-**3** = 8:1. Further experiments indicated that an equilibrium of these geometrical isomers is reached even at room temperature within a few hours. The azide **3** is stable in boiling toluene and shows no tendency to undergo transformation to the

vinyl azide **4**. The fact that the product obtained has the structure of allyl azide **3** and is definitely not **4** is proved unequivocally not only by $^1$H NMR spectra, showing appropriate signal integrals, but also by coupled $^{13}$C NMR spectra. The only sp$^3$ hybridized carbon atom of (*E*)-**3** gives rise to a doublet at $\delta = 72.1$ with $^1J = 142.5$ Hz, while the analogous carbon of (*Z*)-**3** gives a doublet at $\delta = 62.9$ with $^1J = 143$ Hz.

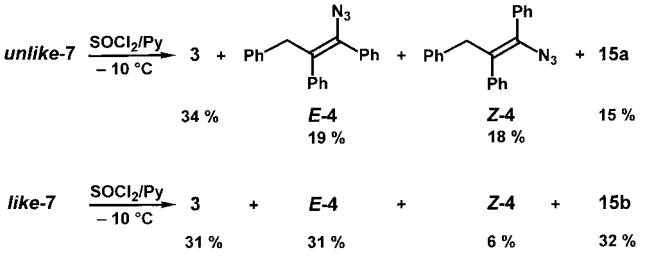
The allyl azide **3** not only exhibits similar stability as was described for (*E*)-**4** by Bowie, Nussey, and Ward,[5] but its analytical and spectroscopic data also match those of what they believed to be (*E*)-**4**. When **1**[7] was treated with **2**[18] as reported,[5] the resulting azide proved to be identical to the **3** obtained from (*E*)-**10** and sodium azide or from (*E*)-**11** and hydrazoic acid. These findings prove that Bowie, Nussey, and Ward[5] erroneously[19] assigned the structure (*E*)-**4** to the compound (*E*)-**3** and that a rearrangement of allyl azide **3** to produce the vinyl azide (*E*)-**4** is not to be expected.

Consequently, dehydration of *unlike*-**7** should not yield (*E*)-**4** but the azide **3** should be formed instead. In order to prove this, the alkenes (*E*)-**5** and (*Z*)-**5** were allowed to react with 3-chloroperbenzoic acid and sodium hydrogen carbonate in dichloromethane to afford the oxiranes *trans*-**6**[5] (85% yield) and *cis*-**6** (93%), respectively (Scheme 3). These epoxides could then be cleaved by $LiAlH_4$ in refluxing THF to give the alcohol **13**.[9,11,20] The results demonstrate that nucleophilic attack on **6** leads regioselectively to tertiary alcohols. Thus, cleavage of *trans*-**6** proceeds upon treatment with sodium azide in aqueous DMF to produce *unlike*-**7**[5] (150°C/9−19 d, 92% yield), while *like*-**7** may be prepared from *cis*-**6** and sodium azide in aqueous ethanol (100°C/5 d, 61−72%). After dehydration of *unlike*-**7** using methanesulfonyl chloride and sulfur dioxide[21] in DMF and pyridine according to the published procedure,[5] chromatographic workup furnishes the allyl azides **3** (41% yield), azirine **14** (16%), the chloride **15a** (19%), and the starting material *unlike*-**7** (14%). The analogous reaction of *like*-**7** furnishes **3** (22%), **14** (7%), **15b** (20%), and recovered *like*-**7** (3%). The generation of **15** proceeds stereospecifically since **15a** is only formed from *unlike*-**7** whereas **15b** is only observed starting from *like*-**7**. We have not been able to clarify whether these substitution reactions proceed with retention or inversion of the configuration.

The structures of **15a** and **15b** have been verified not only by their spectroscopic data, but also by carrying out elimination reactions with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in benzene at 60°C. Upon treatment with this base, **15a** gives **3** and **14**, while **15b** is exclusively transformed into **14**. Clearly, azirine **14** represents a thermal decomposition product of (*E*)-**4** or (*Z*)-**4**, which should possess a low stability akin to that of **8**. The generation of **14** upon dehydration of *unlike*-**7** or *like*-**7** can also be explained by invoking the short-lived intermediate **4**.

The structure of the heterocycle **14** has been confirmed by its spectroscopic data and further corroborated by an independent synthesis involving a Neber rearrangement. Thus, the ketone **16**[22] was converted into the hydrazone **17** by heating with *N,N*-dimethylhydrazine at 180°C (yield 58−66%), which was then methylated with methyl iodide at 80°C to give the hydrazonium salt **18** (96%).[23] On treatment with sodium 2-propanolate in propan-2-ol at 37−40°C, **18** was converted into **14** in 38% yield.

Our results suggested that the unstable vinyl azides **4** could probably be directly observed for the first time if dehydration of **7** could be performed at even lower temperatures. To this end, *unlike*-**7** was treated with thionyl chloride in pyridine at −10°C (Scheme 4) to furnish a mixture of **3** (34% yield), (*E*)-**4** (19%), (*Z*)-**4** (18%), and **15a** (15%). When the workup was performed rapidly at low temperatures, or when the reaction was run in [D$_5$]pyridine and analyzed by $^1$H NMR spectroscopy, the proportion of (*Z*)-**3** was found to be greater than that of (*E*)-**3**, e.g. (*E*)-**3**/(*Z*)-**3** = 1:2, indicating that the equilibration of the allyl azides **3** was not complete. The products could be partly separated by HPLC and unequivocally characterized spectroscopically. For example, the $^1$H- and $^{13}$C NMR spectra of **4** correspond well to the structures of vinyl azides and differ markedly from the data published in ref.[5]. The thermal stabilities of azides **4** are considerably lower than those of **3**. On storage at room temperature, both (*E*)-**4** (half-life 9.0 h at 30°C) and (*Z*)-**4** (half-life ca. 28 h) are converted into **14** (yield 96−98%). The different conversion rates are in accordance with the relative thermal stabilities of **8** and its geometrical isomer.[7][8] The transformations of (*E*)-**4** and (*Z*)-**4** can also be realized by photolysis (yields 84−90%), although **14** is degraded upon prolonged irradiation. Analogous treatment of *like*-**7** with thionyl chloride and pyridine gives a mixture of **3** (31% yield), (*E*)-**4** (31%), (*Z*)-**4** (6%), and **15b** (32%). The formation of **15** from **7** is again stereospecific.




Scheme 4. Products obtained upon treatment of azido alcohols **7** with thionyl chloride and pyridine

## Sigmatropic, Photolytic, and Prototropic Isomerization of Azides

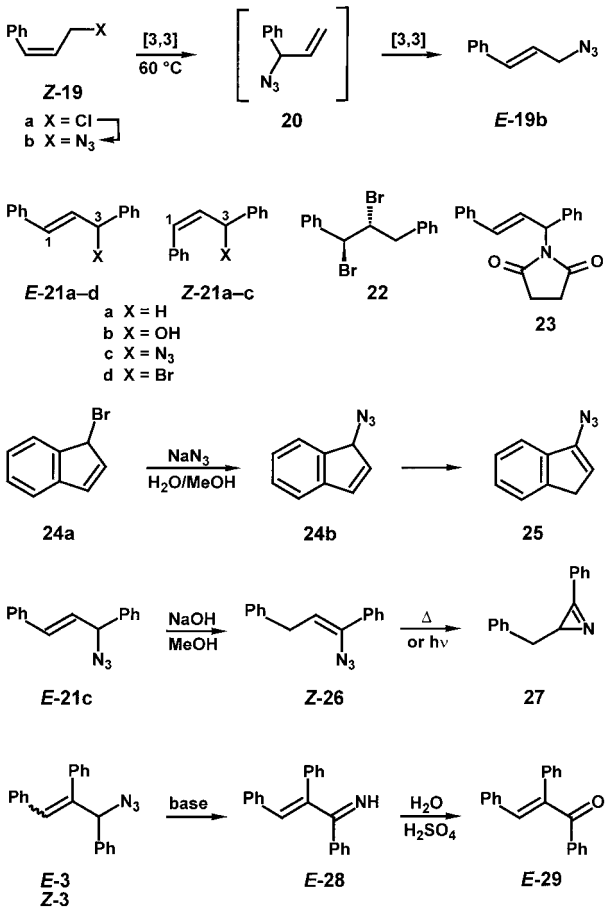
The azide **3** is found to consist purely of the (*E*) isomer if it is analyzed by NMR spectroscopy immediately after recrystallization. However, the equilibrium with (*E*)-**3**/(*Z*)-**3** = 8:1 is re-established within a few hours when the substance is stored in solution at room temperature. Separation of the (*Z*) isomer by HPLC and its subsequent equilibration confirm the reversible nature of the process, which is based on a [3,3] sigmatropic rearrangement of the azido group.

A smooth [3,3] migration of an azido group was first discovered by Winstein[24] in the case of some simple allylic

compounds. This type of rearrangement reaction may be the reason for other equilibrations of geometrical isomers,[25] although somewhat divergent interpretations have been given in the literature.[26] For example, the azide (*Z*)-**19b**, easily accessible from the chloride (*Z*)-**19a**,[27] rearranges irreversibly to the *trans* isomer (*E*)-**19b** on heating in solution at 60°C (Scheme 5), for which a mechanism proceeding via the short-lived intermediate **20** is plausible. On irradiation of (*E*)-**19b** in the presence of acetophenone, a photochemical equilibrium between (*E*)-**19b** and (*Z*)-**19b** is attained.[28] However, the yield of (*Z*)-**19b** is limited to 22% due to decomposition of the azides caused by UV radiation. The azide (*E*)-**21c**,[29] smoothly accessible from (*E*)-**21d** and sodium azide, can be similarly isomerized, although the yield of (*Z*)-**21c** is very low and the thermal back-reaction to give (*E*)-**21c** occurs even at room temperature. The structure of (*Z*)-**21c** was proven not only by its $^1$H NMR data (Table 1), but also by the irreversible [3,3] sigmatropic rearrangement (*Z*)-**21c** → (*E*)-**21c**. On treatment of (*E*)-**21b** with hydrogen bromide according to the published procedure,[30][31] the bromide (*E*)-**21d** is produced. Reaction of (*E*)-**21a** with *N*-bromosuccinimide and azodiisobutyronitrile in dry carbon tetrachloride has been found not to lead to **21d**, despite the claims of two independent reports.[32] Instead, the products of this reaction are found to be **22** and **23**, as was shown in a previously published article.[33a] Furthermore, the $^1$H NMR data attributed[32a] to **21d** are not compatible with the structure of this bromide (*cf.* the data in Table 1). When **22**[33] is treated with an excess of sodium azide in DMSO, (*Z*)-**26** is formed almost quantitatively.

Base-catalyzed rearrangement reactions of allyl azides to give vinyl isomers have rarely been mentioned in the literature.[2d,4] In favorable cases, where substrates possess acidic protons, they can be isomerized under mild conditions to produce vinyl azides in high yields. For example, treatment of 1-bromo-1*H*-indene (**24a**)[34] with sodium azide in aqueous methanol leads to the azide **25** in 91% yield as a result of substitution and subsequent migration of the C,C double bond. After a short reaction time (1 h/20°C), the same starting materials afford 1-azido-1*H*-indene (**24b**) in 95% yield.[35] A stronger base such as sodium hydroxide in methanol is necessary to bring about the prototropic rearrangement of (*E*)-**21c** to the vinyl azide (*Z*)-**26**. The constitution of (*Z*)-**26** has been proved not only by its spectroscopic data, but also by its thermal or photochemical transformation into azirine **27**. The generation of this heterocycle is at variance with ref.[36], in which the pyrolysis of (*E*)-**26** as well as of (*Z*)-**26** was reported to give "mixtures of many products". These did not include **27** or other decay products of **26**.

We have not succeeded in carrying out a base-catalyzed isomerization of **3**. Using $NaN_3$, 1,4-diazabicyclo[2.2.2]octane, NaOMe, NaOEt, or *tert*-octylimino-tris(dimethylamino)phosphorane (phosphazene base, $P_1$-*t*Oct, Fluka), no reaction was observed. On heating or on treatment with stronger bases such as KO*t*Bu or the phosphazene base $P_4$-*t*Bu (Fluka), **3** undergoes nitrogen loss to give the imine **28**.




Scheme 5. Syntheses of allylic azides and their [3,3] sigmatropic, photolytic (*cis*−*trans*), or base-catalyzed (prototropic) isomerizations

Neither the vinyl azide **4** nor its secondary product **14** could be detected. The imine **28** thus formed was mainly of the (*E*) configuration, as shown by hydrolysis which led to the known[37] ketone (*E*)-**29**.[38]

## Assignment of Configurations by means of $^1$H NMR Spectroscopic Data

Substitution reactions are not suitable for making assignments of the geometrical configurations of **3** and (*E*)-**10** since these transformations proceed with retention as well as inversion of the configuration of the alkene, as exemplified by the syntheses and successive reactions of (*E*)-**10** (Scheme 2). In Table 1, the $^1$H NMR spectra of **3** and (*E*)-**10** are compared with those of **5**, **11**, **21a**,[39] **21b**,[39] **21c**, and (*E*)-**21d**. The configuration determinations of the compounds included for comparison purposes, **5** and **11**, have been reported in the literature.[9,11,12,14] In the case of **21a−d**, the assignments of the *cis* and *trans* isomers were unequivocally made with the help of the vicinal coupling constants of the alkene substructures. The terminal phenyl group in the *cis* position relative to the carbon atom with $sp^3$ hybridization (C-3) clearly induces an additional deshielding effect on the signal due to 3-H in (*E*)-**5**, (*Z*)-**11**,

Table 1. $^1$H NMR spectroscopic data (δ and *J* values) for polyphenylprop-1-enes[a]

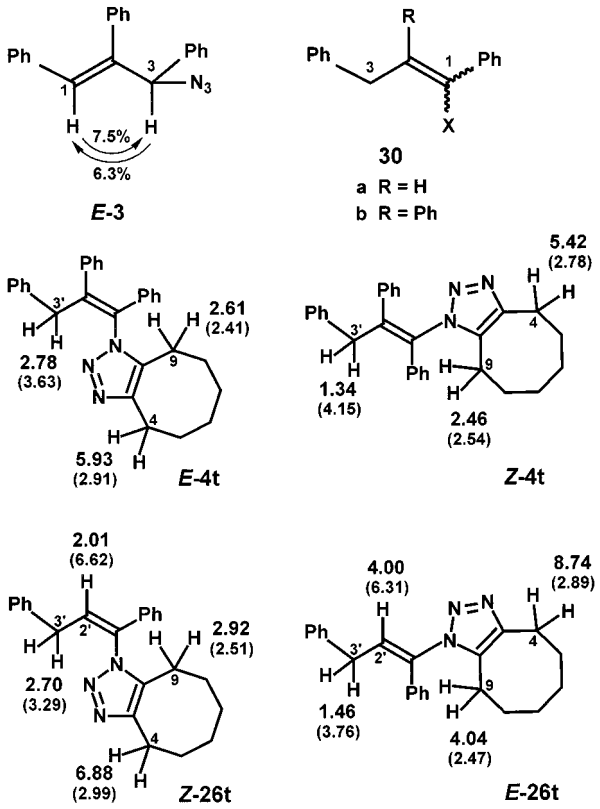
| compound | δ(3-H)[b] | other data |
|---|---|---|
| (*E*)-**3** | 5.46 (s) | 6.83 (s, 1-H), 6.89−7.41 (m, 15 H) |
| (*Z*)-**3** | 6.21 (s) | 7.11−7.43 (m, 16 H) |
| (*E*)-**5** | 4.14 (s) | 7.12 (s, 1-H), 7.15−7.38 (m, 13 H), 7.47−7.52 (m, 2 H) |
| (*Z*)-**5** | 3.78 (s) | 6.44 (s, 1-H), 6.90−6.95 (m, 2 H), 7.04−7.30 (m, 13 H) |
| (*E*)-**10** | 6.04 (s) | 6.84−7.54 (m, 16 H) |
| (*E*)-**11** | 5.55 (br. d, $^3J$ = 4.3 Hz) | 2.17 (br. d, $^3J$ = 4.3 Hz, OH), 6.87 (s, 1-H), 6.90−7.41 (m, 15 H) |
| (*Z*)-**11** | 6.19 (d, $^3J$ = 6.7 Hz) | 2.09 (d, $^3J$ = 6.7 Hz, OH), 7.03 (s, 1-H), 7.21−7.48 (m, 15 H) |
| (*E*)-**21a** | 3.55 (d, $^3J$ = 6.4 Hz) | 6.37 (dt, $^3J$ = 15.8 Hz, $^3J$ = 6.5 Hz, 2-H), 6.45 (br. d, $^3J$ = 15.8 Hz, 1-H), 7.26−7.55 (m, 10 H) |
| (*Z*)-**21a** | 3.68 (dd, $^3J$ = 7.4 Hz, $^4J$ = 1.6 Hz) | 5.86 (dt, $^3J$ = 11.6 Hz, $^3J$ = 7.5 Hz, 2-H), 6.60 (dt, $^3J$ = 11.5 Hz, $^4J$ = 1.7 Hz, 1-H), 7.15−7.42 (m, 10 H) |
| (*E*)-**21b** | 5.39 (d, $^3J$ = 6.6 Hz) | 1.73 (br. s, OH), 6.38 (dd, $^3J$ = 15.9 Hz, $^3J$ = 6.6 Hz, 2-H), 6.69 (d, $^3J$ = 15.9 Hz, 1-H), 7.2−7.4 (m, 10 H) |
| (*Z*)-**21b** | 5.64 (d, $^3J$ = 9.3 Hz) | 1.93 (br. s, OH), 5.93 (dd, $^3J$ = 11.1 Hz, $^3J$ = 9.3 Hz, 2-H), 6.69 (d, $^3J$ = 11.1 Hz, 1-H), 7.2−7.5 (m, 10 H) |
| (*E*)-**21c** | 5.22 (d, $^3J$ = 7.3 Hz) | 6.30 (dd, $^3J$ = 15.7 Hz, $^3J$ = 7.3 Hz, 2-H), 6.72 (d, $^3J$ = 15.7 Hz, 1-H), 7.19−7.44 (m, 10 H) |
| (*Z*)-**21c** | 5.46 (d, $^3J$ = 10.0 Hz) | 5.92 (dd, $^3J$ = 11.4 Hz, $^3J$ = 10.0 Hz, 2-H), 6.86 (d, $^3J$ = 11.4 Hz, 1-H), 7.0−7.6 (Ph) |
| (*E*)-**21d** | 5.85 (br. d, $^3J \approx 9$ Hz) | 6.61 (br. d, $^3J \approx 16$ Hz, 1-H), 6.73 (br. m, 2-H), 7.3−7.5 (m, 10 H) |

[a] Measured in $CDCl_3$ at 300 or 400 MHz; internal standard TMS (δ = 0); *J* in Hz. − [b] All compounds were considered as prop-1-enes with 3-H bound to the $sp^3$ hybridized carbon.

(*Z*)-**21a**, (*Z*)-**21b**, and (*Z*)-**21c**, with Δδ = 0.36, 0.64, 0.13, 0.25, and 0.24 ppm, respectively, compared to the corresponding geometrical isomers. An analogous low-field shift with Δδ = 0.75 ppm for the signal of 3-H in (*Z*)-**3** is also consistent with these results. Furthermore, homonuclear NOE difference spectra prove the configuration of (*E*)-**3** (Scheme 6).

In the case of simple primary allyl,[25][40] benzyl,[41] or cinnamyl[41a,42] derivatives, the deshielding effect of functional groups on protons located on the same carbon atom increases in the order OH > Br > $N_3$. However, secondary isopropyl,[43] 1-methylprop-2-enyl[25,40b,44], and benzhydryl[45] compounds show the following order of deshielding: Br > OH ≈ $N_3$. The same is true for the chemical shifts of the α protons (3-H) in (*E*)-**21d**, (*E*)-**21b**, and (*E*)-**21c**, which are structurally similar to (*E*)-**10**, (*E*)-**11**, and (*E*)-**3**. Thus, the (*E*) configuration is assigned to the bromide **10** on the basis of a comparison of its $^1$H NMR data with those of **3** and **11**. The $^1$H NMR spectrum of unknown (*Z*)-**10** would be expected to show δ(3-H) > 6.21.

In the case of compounds of type **30** with X ≠ H, the influence of X and the phenyl group at C-1 on the chemical shift of the 3-H signal is not as straightforward as might appear considering the compounds in Table 1. Thus, the configurations of compounds **30** cannot easily be correlated with the δ values of 3-H, as shown, for example, by considering the data for **30a** with X = Me,[46] X = F,[47] X = Cl,[48] and X = Br[49] or **30b** with X = Me,[50] X = Bu,[9] X = $CH_2Ph$,[51] and X = Cl.[10] Thus, we set out to prove the configuration of **4** using a lanthanide shift reagent. Since the $^1$H NMR spectra of azides, with the exception of those of a few special compounds,[52] are nearly unaffected[25] by such shift reagents, the substrates (*E*)-**4**, (*Z*)-**4**, (*E*)-**26**, and (*Z*)-**26** were treated with cyclooctyne[53] to give (*E*)-**4t**, (*Z*)-**4t**, (*E*)-**26t**, and (*Z*)-**26t**, respectively. These derivatives form strong complexes with europium(III) tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione), $Eu(fod)_3$, as a result of interactions between the unshared electron pairs of N-2 and N-3 of the 1*H*-triazoles and the paramagnetic reagent. Therefore, large deshielding




Scheme 6. NOE enhancements observed for the $^1$H NMR signals of (*E*)-**3** and results derived from $^1$H NMR spectra of **4t** and **26t** measured in the presence of $Eu(fod)_3$; numbers in parentheses correspond to chemical shifts (δ) in the absence of $Eu(fod)_3$, while the numbers above these data indicate Δδ·[azide]/[$Eu(fod)_3$]

effects are observed on the signals of 4-H and to a lesser degree on those of 9-H, whereas simple hydrocarbons such as (*E*)-**21a** lead to low-field shifts at least two hundred times smaller. Clearly, the chemical shifts of 3′-H of (*E*)-**4t** and (*Z*)-**26t** are significantly more affected than those of (*Z*)-**4t** and (*E*)-**26t**, while the Δδ value of 2′-H of (*Z*)-**26t** is distinctly lower than that of (*E*)-**26t**. It is possible to envisage stretched conformations, with the whole propenyl chain and the bulky eight-membered ring arranged on opposite sides as shown in Scheme 6, since homonuclear NOE difference spectra do not show any evidence for nuclear Overhauser effects between 9-H and 2′-H or 3′-H.

## Conclusion

In summary, we have shown that the structure of vinyl azide (*E*)-**4** was erroneously assigned to the allylic azides **3**. Thus, the generation of these substances from azirine **1** and diazo compound **2**, as well as their chemical and spectroscopic properties lose their incompatibilities when the correct structures are taken into consideration. These findings are further confirmed by the first isolation of the vinyl azides (*E*)-**4** and (*Z*)-**4**, which exhibit markedly different thermal stability to the isomeric compounds **3**.

## Experimental Section

**General Remarks:** Melting points (uncorrected): Büchi 510 apparatus. − Elemental analyses: Firma Beller, Göttingen, and Vario EL Elementar Analysensysteme GmbH (Hanau); elemental analyses of azides were not performed in view of their instability and explosive decomposition. − IR: Beckman Acculab 4 and Bruker IFS 28. − UV/Vis: Beckman Acta M VII. − $^1$H NMR: Varian EM-360 (60 MHz) and Gemini 300 (300 MHz), Bruker WP 80 (80 MHz) and WH 400 (400 MHz); internal standard TMS (δ = 0). − $^{13}$C NMR: Varian Gemini 300 (75 MHz) and Bruker WH 400 (100.6 MHz); internal standard TMS (δ = 0) or solvent signals recalculated relative to TMS. The multiplicities were determined with the aid of *gated* spectra and/or DEPT 135 experiments. − $^{15}$N NMR: Bruker WH 400 (40.53 MHz); external standard $CH_3NO_2$ (δ = 0). − MS (EI): Varian MAT 112. − MS (HR-EI): Varian MAT 311 A. − HPLC: Knauer HPLC pump 64, Knauer variable-wavelength monitor. − Photolyses: Irradiations were performed at −30 to 0°C using a high-pressure mercury lamp (TQ 150, Quarzlampengesellschaft Hanau) supplied with glass or quartz equipment and an ethanol cryostat.

**(*E*)-3-Bromo-1,2,3-triphenyl-1-propene [(*E*)-10] from 5:** A solution of (*Z*)-**5**,[9][11] (*E*)-**5**,[9][11] or a mixture of both (4.00 g, 14.8 mmol) in dry $CCl_4$ (15 mL) was treated with *N*-bromosuccinimide (2.67 g, 15.0 mmol) and azodiisobutyronitrile (30 mg) and refluxed until the liberation of succinimide, insoluble in $CCl_4$, had ceased. The reaction mixture was then cooled, the precipitate was filtered off, and the filtrate was concentrated in vacuo to afford a light-yellow oil. The product, which solidified on standing, was purified by crystallization from pentane to give 3.72 g of (*E*)-**10** (72%) as a beige solid, m.p. 72°C. − IR ($CCl_4$): $\tilde{\nu}$ = 3090 cm$^{-1}$, 3070, 3030, 1600, 1495, 1450, 1080, 1035, 925. − UV/Vis (cyclohexane): $\lambda_{max}$ (lg ε) = 228.5 nm (4.17), 267 (4.13). − $^{13}$C NMR ($CDCl_3$): δ = 60.77 (d, *J* = 153 Hz, C-3), 127.38, 127.64, 127.91, 128.10, 128.23, 128.40, 128.66, 129.32, 129.66, 131.65, 135.80 (s), 137.91 (s), 139.05 (s), 141.35. In some cases, especially after contact with a metal spatula, solid (*E*)-**10** slowly evolved hydrogen bromide, eventually leading to an almost quantitative yield of **12**.[13][15]

**(*E*)-3-Bromo-1,2,3-triphenyl-1-propene [(*E*)-10] from (*E*)-11:** To a stirred solution of (*E*)-**11** (7.15 g, 25.0 mmol) in dry benzene (75 mL) at 0−5°C, phosphorus tribromide (4.32 g, 16.0 mmol) was added dropwise over a period of 10 min. The resulting mixture was stirred at this temperature for a further 30 min, then poured into ice/water and extracted three times with diethyl ether. The combined organic layers were washed with saturated aqueous sodium hydrogen carbonate solution and dried with $MgSO_4$. After removal of the solvent in vacuo, the residue solidified to yield 8.70 g (100%) of (*E*)-**10**, which proved identical to the product obtained from **5** and *N*-bromosuccinimide.

Starting from (*Z*)-**11**, analogous treatment with phosphorus tribromide gave (*E*)-**10** in 89% yield.

**(*Z*)-1,2,3-Triphenyl-1-propene [(*Z*)-5] from (*E*)-10:** To a stirred suspension of $LiAlH_4$ (1.00 g, 26.4 mmol) in dry diethyl ether (100 mL) at room temperature, a solution of (*E*)-**10** (2.85 g, 8.16 mmol) in dry diethyl ether (20 mL) was added dropwise over a period of 30 min. The resulting mixture was stirred for a further 16 h and then hydrolyzed by the dropwise addition of water until hydrogen evolution ceased. The white precipitate was collected by suction filtration and extracted with diethyl ether. After drying the combined organic layers with $MgSO_4$, evaporation of the solvent afforded 2.15 g (97%) of **5** with (*E*)/(*Z*) = 5:95 as shown by $^1$H NMR.

**(*Z*)-5:** $^{13}$C NMR ($CDCl_3$): δ = 46.94 (t, C-3), 126.14, 126.31, 126.86, 127.79, 128.10, 128.22, 128.34, 128.59, 129.00, 129.19, 137.18 (s), 139.12 (s), 141.04 (s), 142.08 (s).

**(*E*)-5:** $^{13}$C NMR ($CDCl_3$): δ = 36.11 (t, C-3), 125.87, 126.43, 126.89, 127.18, 128.26, 128.28, 128.29, 128.42, 128.53, 130.21, 137.69 (s), 139.07 (s), 139.60 (s), 142.37 (s).

**Hydrolysis of (*E*)-10:** To a solution of (*E*)-**10** (0.75 g, 2.15 mmol) in dioxane (60 mL) was added a solution of sodium hydroxide (100 mg, 2.50 mmol) in water (10 mL). The resulting mixture was stirred for 5 d at room temperature, then poured into ice/water and extracted three times with diethyl ether. The combined organic layers were washed three times with water and dried with $MgSO_4$. Removal of the solvent in vacuo gave 0.49 g (80%) of (*E*)-**11**, m.p. 85−87°C (pentane/diethyl ether). − UV/Vis (cyclohexane): $\lambda_{max}$ (lg ε) = 227 nm (4.26), 259 (4.23). − $^{13}$C NMR ($CDCl_3$): δ = 79.12 (d, *J* ≈ 146 Hz, CHOH), 126.79, 126.83, 127.15, 127.31, 127.62, 127.87, 128.23, 128.42, 129.27, 129.40, 136.34 (s), 138.01 (s), 141.65 (s), 143.90 (s).

The product proved to be identical to (*E*)-**11** synthesized by literature methods[12][13] on the basis of its UV/Vis, $^1$H NMR and $^{13}$C NMR spectra.

**(*E*)- and (*Z*)-3-Azido-1,2,3-triphenyl-1-propene [(*E*)-3 and (*Z*)-3] from (*E*)-10:** A solution of sodium azide (26.0 g, 400 mmol) in water (120 mL) and ethanol (400 mL) was added to (*E*)-**10** (10.4 g, 29.8 mmol). Alternatively, the reaction could be performed in DMF instead of water/ethanol. The mixture was stirred for 5 d at room temperature and then poured into ice/water. The organic layer was separated, and the aqueous layer was extracted three times with diethyl ether. The combined organic extracts were washed three times with water and dried with $MgSO_4$. After removal of the solvent in vacuo, the residue solidified to yield 7.20 g (78%) of **3** with (*E*)/(*Z*) = 8:1 as shown by $^1$H NMR. When **3** was

recrystallized from pentane, the $^1$H NMR spectrum measured as soon as possible thereafter indicated only (*E*)-**3** and no signals due to (*Z*)-**3** were apparent. However, the equilibrium of (*E*)-**3** and (*Z*)-**3** was established within 2 h at room temperature. The geometrical isomers could be separated by HPLC {LiChrospher Si 60 (5 μm), 2 cm Ø × 20 cm, diethyl ether/hexane, 1:40, flow rate 8 mL/min, $t_R$ [(*Z*)-**3**] = 23 min, $t_R$ [(*E*)-**3**] = 29 min}. The fractions had to be cooled to avoid equilibration.

**(*E*)-3**: Colorless solid, m.p. (pentane) 65°C. − IR ($CCl_4$): $\tilde{\nu}$ = 2110 $cm^{-1}$. − UV/Vis (cyclohexane): $\lambda_{max}$ (lg ε) = 227.5 nm (4.23), 260 nm (4.20). − $^{13}$C NMR ($CDCl_3$): δ = 72.12 (d, *J* = 142.5 Hz, C-3), 127.19 (d), 127.45 (d), 127.47 (d), 127.91 (d), 128.03 (d), 128.38 (d), 128.41 (d), 129.17 (d), 129.33 (d), 129.59 (d), 135.71 (s), 137.24 (s), 137.64 (s), 139.83 (s).

**(*Z*)-3**: $^{13}$C NMR ($CDCl_3$, −20°C): δ = 62.91 (d, *J* = 143 Hz, C-3), 126.42 (d), 127.38 (d), 127.66 (d, 2 C), 127.93 (d), 128.01 (d), 128.47 (d), 128.65 (d), 128.67 (d), 134.14 (d), 136.03 (s), 137.65 (s), 138.13 (s), 138.27 (s).

**(*E*)- and (*Z*)-3-Azido-1,2,3-triphenyl-1-propene [(*E*)-3 and (*Z*)-3] from (*E*)-11:** To a stirred suspension of sodium azide (0.61 g, 9.4 mmol) in $CHCl_3$ (6 mL) at 0°C, concentrated $H_2SO_4$ (1.1 mL, 20.5 mmol) was added dropwise, followed by a solution of (*E*)-**11** (2.00 g, 6.98 mmol) in $CHCl_3$. The resulting mixture was stirred for a further 60 min at 0°C, then poured into ice/water and diluted with diethyl ether. The organic layer was washed with saturated aqueous $NaHCO_3$ solution, dried with $MgSO_4$, and concentrated to dryness. The residue (0.85 g) was found to consist of **3** (0.55 g, 25%) and **12** (0.30 g, 16%), as shown by its $^1$H- and $^{13}$C NMR spectra.

**(*E*)- and (*Z*)-3-Azido-1,2,3-triphenyl-1-propene [(*E*)-3 and (*Z*)-3] from 1 and 2:** When **1**[7] in diethyl ether was treated with **2**[18] in cyclohexane, as described in the literature,[5] the azides (*E*)-**3** and (*Z*)-**3** were isolated after removal of the solvents and purification of the residue by chromatography. The products were shown to be identical to the (*E*)-**3** and (*Z*)-**3** obtained from (*E*)-**10** or (*E*)-**11** by comparison of their m.p. and IR data, as well as by complete matching of their $^1$H- and $^{13}$C NMR spectra.

***trans*-2-Benzyl-2,3-diphenyloxirane (*trans*-6):** A mixture of *m*-chloroperbenzoic acid and $NaHCO_3$ in dry $CH_2Cl_2$ was added to a solution of (*E*)-**5**[9][11] in $CH_2Cl_2$ and the resulting mixture was stirred at room temperature as described in ref.[5] After workup and purification by chromatography, *trans*-**6** was isolated in 85% yield; m.p. 62.5°C (pentane), which is significantly different to the value quoted in ref.[5] (48−49°C). − IR ($CCl_4$): $\tilde{\nu}$ = 3090 $cm^{-1}$, 3070, 3030, 1600, 1495, 1450, 1260, 1075, 1030, 945. − $^1$H NMR ($CDCl_3$): δ = 2.84 (d, $^2J$ = 15.1 Hz, 1 H), 3.18 (d, $^2J$ = 15.1 Hz, 1 H), 4.04 (s, 3-H), 7.0−7.5 (m, 15 H). The diastereotopic protons of the benzyl group were found not to lead to one singlet as had been claimed in ref.[5] Even in the 60 MHz $^1$H NMR spectrum, the benzylic protons of *trans*-**6** gave rise to a pair of well-resolved doublets. − $^{13}$C NMR ($CDCl_3$): δ = 36.26 (t), 66.44 (d), 67.00 (s), 126.17, 126.24, 126.63, 127.35, 127.89, 128.02, 128.17, 128.31, 129.56, 135.74 (s), 136.99 (s), 140.46 (s).

When *trans*-**6** was treated with an excess of $LiAlH_4$ in dry THF (16 h, reflux), the resulting product was shown to be **13** by comparing its $^1$H NMR spectrum with known data.[11]

***cis*-2-Benzyl-2,3-diphenyloxirane (*cis*-6):** The alkene (*Z*)-**5** was treated with *m*-chloroperbenzoic acid and $NaHCO_3$ in dry $CH_2Cl_2$ according to the procedure described in ref.[5] for the synthesis of *trans*-**6**. After workup, *cis*-**6** was isolated as a colorless solid in 93% yield; m.p. 77−78.5°C (pentane). − $^1$H NMR ($CDCl_3$): δ = 3.26 (d, $^2J$ = 14.2 Hz, 1 H), 3.35 (d, $^2J$ = 14.2 Hz, 1 H), 4.13 (s, 3-H), 6.9−7.3 (m, 15 H). − $^{13}$C NMR ($CDCl_3$): δ = 45.19 (t), 63.78 (d, C-3), 69.11 (s, C-2), 126.50, 126.67, 127.08, 127.33, 127.52, 127.57, 127.91, 128.15, 130.08, 135.45 (s), 136.13 (s), 136.76 (s). − $C_{21}H_{18}O$ (286.4): calcd. C 88.08, H 6.34; found C 88.11, H 6.27.

On treatment of *cis*-**6** with $LiAlH_4$ in THF (16 h, reflux), **13** was obtained.

***unlike*-1-Azido-1,2,3-triphenylpropan-2-ol (*unlike*-7):** A solution of *trans*-**6** (1.00 g, 3.49 mmol) and sodium azide (2.42 g, 37.2 mmol) in DMF (10 mL) and water (10 mL) was heated in a sealed glass ampoule at 150°C for 9−19 d. Thereafter, the mixture was diluted with water and extracted repeatedly with diethyl ether. The combined organic layers were washed with water, dried over $MgSO_4$, and concentrated to dryness to yield 1.06 g (92%) of *unlike*-**7**. The product was purified by chromatography ($SiO_2$) to give a colorless solid; m.p. 102−104°C (diethyl ether/pentane). − IR ($CCl_4$): $\tilde{\nu}$ = 3570 $cm^{-1}$ (OH), 3090, 3070, 3040, 2925, 2860, 2105 ($N_3$), 1600, 1495, 1450. − $^1$H NMR ($CDCl_3$): δ = 2.31 (s, OH), 3.41 (d, $^2J$ = 13.8 Hz, 3-H), 3.42 (d, $^2J$ = 13.8 Hz, 3-H), 4.87 (s, 1-H), 6.88−7.50 (m, 15 H). − $^{13}$C NMR ($CDCl_3$): δ = 45.46 (t, C-3), 73.63 (d, C-1), 79.18 (s, C-2), 126.40, 126.69, 126.94, 127.57, 127.86, 128.01, 128.13, 129.12, 130.70, 135.33 (s), 135.50 (s), 141.25 (s).

When *trans*-**6** was treated with sodium azide in DMSO/ethanol at 68°C for 14 h, as described in ref.,[5] no reaction product could be detected. At higher temperatures, however, the reagent $NaN_3$/DMSO induced the decomposition of *trans*-**6**.

***like*-1-Azido-1,2,3-triphenylpropan-2-ol (*like*-7):** A solution of *cis*-**6** (3.10 g, 10.8 mmol) and sodium azide (7.50 g, 115 mmol) in ethanol (90 mL) and water (30 mL) was heated at 100°C for 5 d. Workup was carried out as described in the case of *unlike*-**7**. The crude product (2.57 g, 72%) was purified by chromatography ($SiO_2$, diethyl ether/hexane, 1:20) to afford 2.18 g (61%) of *like*-**7** as a yellow solid; m.p. 85.5°C (diethyl ether/pentane). − IR ($CCl_4$): $\tilde{\nu}$ = 2105 $cm^{-1}$ ($N_3$). − $^1$H NMR ($CDCl_3$): δ = 2.26 (s, OH), 3.10 (d, $^2J$ = 13.8 Hz, 3-H), 3.15 (d, $^2J$ = 13.8 Hz, 3-H), 4.83 (s, 1-H), 6.8−7.4 (m, 15 H). In the $^1$H NMR spectrum of *like*-**7** in [$D_6$]DMSO, both the OH and the 1-H proton signals appear as singlets, showing the product to be a tertiary alcohol. − $^{13}$C NMR ($CDCl_3$): δ = 44.29 (t, C-3), 74.06 (d, C-1), 78.67 (s, C-2), 126.45, 126.60, 127.23, 127.71, 127.93, 128.05, 128.54, 129.22, 130.67, 135.36 (s), 135.41 (s), 142.18 (s).

**Reaction of *unlike*-7 with Methanesulfonyl Chloride:** According to the procedure described in ref.,[21] *unlike*-**7** (800 mg, 2.43 mmol) was treated with methanesulfonyl chloride and sulfur dioxide in pyridine and DMF. The conditions had to be changed from 5 min at 10°C to 2.5 h at 45°C since no reaction was observed when the mild conditions mentioned in ref.[5] were used. After workup, the products were separated by chromatography ($SiO_2$, diethyl ether/hexane) and identified by their $^1$H- and $^{13}$C NMR spectra. The order of elution was: **3** (280 mg, 41%), **15a** (160 mg, 19%), **14** (110 mg, 16%), *unlike*-**7** (110 mg, 14%).

Attempts to dehydrate *unlike*-**7** by heating with $H_3PO_4$, TsOH, or $H_2SO_4$ in $CHCl_3$ using a water separator or by treatment with $H_3PO_4$, AcOH/$H_2SO_4$, acidic $Al_2O_3$, $PBr_3$, or TsCl/pyridine were not successful.

**2-Benzyl-2,3-diphenyl-2*H*-azirine (14):** Colorless solid; m.p. 86°C (pentane). − IR ($CCl_4$): $\tilde{\nu}$ = 1735 $cm^{-1}$ (C=N). − $^1$H NMR ($CDCl_3$): δ = 3.52 (d, $^2J$ = 15.0 Hz, 1 H), 3.72 (d, $^2J$ = 15.0 Hz, 1 H), 7.1−7.8 m (15 H). − $^{13}$C NMR ($CDCl_3$): δ = 40.70 (t), 42.30 (s, C-2), 124.73 (s), 126.16, 126.57, 126.60, 128.17, 128.18, 128.95, 129.34, 129.75, 132.69, 137.86 (s), 142.98 (s), 168.51 (s, C-3). − $^{15}$N

NMR ($CDCl_3$): δ = −93.97 (s). − $C_{21}H_{17}N$ (283.35): calcd. C 89.01, H 6.05, N 4.94; found C 88.77, H 6.00, N 4.88.

**1-Azido-2-chloro-1,2,3-triphenyl-1-propene (15a):** Colorless solid; m.p. 76°C (hexane). − IR ($CDCl_3$): $\tilde{\nu}$ = 2110 $cm^{-1}$ ($N_3$). − $^1H$ NMR ($CDCl_3$): δ = 3.69 (s, 2 H), 5.07 (s, 1-H), 6.9−7.3 (m, 15 H). − $^{13}C$ NMR ($CDCl_3$): δ = 47.03 (t, C-3), 74.31 (d, C-1), 80.08 (s, C-2), 126.62, 127.49, 127.59, 127.60, 127.72, 128.17, 128.37, 129.42, 130.95, 134.51, 135.40, 138.12.

A sample of compound **15a** was treated with an excess of DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) in benzene at 60°C for 24 h. The mixture was then diluted with diethyl ether, washed with 5% $H_2SO_4$ and with saturated aqueous $NaHCO_3$ solution, dried over $MgSO_4$, and the solvent was evaporated. $^1H$- and $^{13}C$ NMR spectra showed the residue to consist of the main product **14**, the by-product **3**, and some starting material **15a**.

**Reaction of *like*-7 with Methanesulfonyl Chloride:** The alcohol *like*-**7** (700 mg, 2.13 mmol) was treated with methanesulfonyl chloride and sulfur dioxide in pyridine and DMF for 4.5 h at 45°C according to the procedure for the dehydration of *unlike*-**7**. After workup, the products were similarly separated and identified. Upon chromatography ($SiO_2$), the order of elution was: **3** (145 mg, 22%), **15b** (145 mg, 20%), **14** (40 mg, 7%), *like*-**7** (20 mg, 3%).

**1-Azido-2-chloro-1,2,3-triphenyl-1-propene (15b):** Colorless oil. − $^1H$ NMR ($CDCl_3$): δ = 3.53 (s, 2 H), 5.00 (s, 1-H), 6.9−7.5 (m, 15 H). − $^{13}C$ NMR ($CDCl_3$): δ = 46.16 (t, C-3), 74.28 (d, C-1), 78.87 (s, C-2), 126.79, 127.60, 127.61, 127.96, 128.44, 128.67, 129.05, 129.74, 131.20, 134.47, 135.32, 138.44.

After treatment of **15b** with DBU in benzene at 60°C for 8 d and workup as described in the case of the analogous reaction of **15a**, the residue was found to consist of **14** (60%) and **15b** (40%) as shown by its $^1H$- and $^{13}C$ NMR spectra. Other products, such as **3**, were only present in trace amounts.

**1,2,3-Triphenylpropan-1-one Dimethylhydrazone (17):** A mixture of **16**[22] (19.5 g, 68.1 mmol) and *N,N*-dimethylhydrazine (12 mL, 158 mmol) was heated in a sealed glass ampoule at 180°C for 5 d. After removal of the excess *N,N*-dimethylhydrazine in vacuo, the residue was distilled at 0.001 Torr to give a mixture of **16** and **17**. The whole process of treatment with excess *N,N*-dimethylhydrazine at 180°C followed by distillation was repeated four times to afford 14.78 g of **17** [66% yield, 88% pure ($^1H$ NMR), 58% corrected yield] as a yellow oil, b.p. 155°C/0.001 Torr. − $^1H$ NMR ($CDCl_3$): δ = 2.39 (s, Me), 3.03 (dd, $^2J$ = 14 Hz, $^3J$ = 7 Hz, 3-H), 3.53 (dd, $^2J$ = 14 Hz, $^3J$ = 8 Hz, 3-H), 3.95 (dd, $^3J$ = 8 Hz, $^3J$ = 7 Hz, 2-H), 6.8−7.3 (m, 15 H). − $^{13}C$ NMR ($CDCl_3$): δ = 40.72 (t, C-3), 47.32 (q), 56.28 (d, C-2), 125−130 (several signals), 139.07 (s), 140.79 (s), 141.47 (s), 161.61 (s, C-1).

**1,2,3-Triphenylpropan-1-one *N,N,N*-Trimethylhydrazonium Iodide (18):** A mixture of **17** (14.78 g, 45.0 mmol) and $CH_3I$ (12.50 g, 88.1 mmol) was heated at 80°C for 60 min. The excess $CH_3I$ was then removed in vacuo. This process was completed by adding EtOH and co-evaporating in vacuo. The residue obtained consisted of a brown, glass-like mass of **18** (20.3 g, 96%). − $^1H$ NMR ($CDCl_3$): δ = 3.14 (dd, $^2J$ = 14 Hz, $^3J$ = 8 Hz, 3-H), 3.50 (s, Me), 3.58 (dd, $^2J$ = 14 Hz, $^3J$ = 8 Hz, 3-H), 4.10 (t, $^3J$ = 8 Hz, 2-H), 6.9−7.5 (m, 15 H). − $^{13}C$ NMR ($CDCl_3$): δ = 38.64 (t, C-3), 57.95 (q), 59.60 (d, C-2), 125−130 (several signals), 132.54 (s), 135.74 (s), 140.03 (s), 177.77 (s, C-1).

**2-Benzyl-2,3-diphenyl-2*H*-azirine (14) from 18:** To a stirred solution of sodium (330 mg, 14 mmol) in dry propan-2-ol (90 mL) at 37−40°C, a solution of **18** (7.05 g, 15.0 mmol) in dry propan-2-ol (34 mL) was added dropwise over a period of 30 min. The mixture was stirred at this temperature for a further 45 min and then concentrated in vacuo. The residue was repeatedly extracted with diethyl ether in order to separate the product from the solid sodium iodide. Removal of the solvent from the combined extracts afforded a yellow oil (4.20 g), to which pentane was added. This led to the deposition of **14** (1.60 g, 38%) as a colorless solid, m.p. 86°C (pentane). All spectroscopic data of the product were identical to those of the **14** obtained from (*E*)-**4**, (*Z*)-**4**, *unlike*-**7**, *like*-**7**, **15a**, or **15b**.

**Reaction of *unlike*-7 with Thionyl Chloride:** To a stirred solution of *unlike*-**7** (329 mg, 1.00 mmol) in dry pyridine (3 mL) at −10°C, thionyl chloride (0.145 mL, 1.99 mmol) was added dropwise. The resulting mixture was stirred at this temperature for a further 30 min, then poured into ice/water and extracted with cold diethyl ether. The organic layer was washed with cold 10% aqueous HCl and with cold saturated aqueous $NaHCO_3$, dried with $MgSO_4$ at 0°C, and concentrated in vacuo to furnish a yellow oil (330 mg). $^1H$- and $^{13}C$ NMR spectra indicated that the residue consisted of **3** (34% yield), (*E*)-**4** (19%), (*Z*)-**4** (18%), and **15a** (15%).

When *unlike*-**7** was similarly treated with thionyl chloride in pyridine for 2 h at −10°C, the product distribution differed only slightly. The equilibration of (*E*)-**3** and (*Z*)-**3** was incomplete so that the proportion of (*Z*)-**3** was greater than that of (*E*)-**3** if workup was performed rapidly at low temperature.

The products could be partly separated by HPLC {conditions similar to those used for the separation of (*E*)-**3** and (*Z*)-**3**, $t_R$ [(*E*)-**4**] = 22 min, $t_R$ [(*Z*)-**3**] = 23 min, $t_R$ [(*E*)-**3** + (*Z*)-**4**] = 29 min, $t_R$ (**15a**) = 47 min}.

**Reaction of *like*-7 with Thionyl Chloride:** A solution of *like*-**7** (329 mg, 1.00 mmol) in pyridine was treated with thionyl chloride as described for *unlike*-**7**. Workup gave a yellow oil (326 mg), which was shown to consist of **3** (31% yield), (*E*)-**4** (31%), (*Z*)-**4** (6%), and **15b** (32%) by its $^1H$- and $^{13}C$ NMR data.

**(*E*)-1-Azido-1,2,3-triphenyl-1-propene [(*E*)-4]:** Light-yellow oil. − IR ($CDCl_3$): $\tilde{\nu}$ = 2109 $cm^{-1}$ ($N_3$), 1286. − $^1H$ NMR ($CDCl_3$): δ = 3.99 (s, 3-H), 6.87−6.91 (m, 2 H), 6.96−7.02 (m, 3 H), 7.14−7.25 (m, ca. 10 H). − $^{13}C$ NMR ($CDCl_3$): δ = 39.05 (t, 1 C), 125.93 (d, 1 C), 126.34 (d, 1 C), 127.64 (d, 2 C), 128.26 (d, 2 C), 128.30 (d, 1 C), 128.31 (d, 2 C), 128.50 (d, 2 C), 128.83 (s, 1 C), 129.59 (d, 2 C), 129.77 (d, 2 C), 133.70 (s, 1 C), 134.57 (s, 1 C), 139.47 (s, 1 C), 139.92 (s, 1 C).

**(*Z*)-1-Azido-1,2,3-triphenyl-1-propene [(*Z*)-4]:** $^1H$ NMR ($CDCl_3$): δ = 3.64 (s, 3-H), 6.97−ca. 7.50 (m, Ph). − $^{13}C$ NMR ($CDCl_3$): δ = 39.83 (t, C-3), 125.91 (d), 127.10 (d), 127.33 (s), 127.92 (d), 128.11 (d), 128.45 (d?), 128.89 (d), 129.03 (d), 129.04 (d), 129.07 (d), 133.72 (s), 134.33 (s), 138.77 (s), 139.25 (s).

**2-Benzyl-2,3-diphenyl-2*H*-azirine (14) from (*E*)-4 or (*Z*)-4:** Solutions of (*E*)-**4** or (*Z*)-**4** in $CDCl_3$ were stored at room temperature or heated at 30°C in a thermostat; yields of **14**: 96% from (*E*)-**4**, 98% from (*Z*)-**4** ($^1H$ NMR). When such solutions of the azides were irradiated using a high-pressure mercury lamp, **14** was obtained in 90% yield based on 84% conversion of (*E*)-**4** and in 84% yield based on 73% conversion of (*Z*)-**4** ($^1H$ NMR). On prolonged irradiation, **14** was degraded to give a multi-component mixture. One of the main products was possibly 3-benzyl-2-phenyl-1*H*-indole,[54] tentatively assigned on the basis of the $^1H$ NMR spectrum.

**(*Z*)-(3-Azidoprop-1-enyl)benzene [(*Z*)-19b]:** A solution of sodium azide (1.48 g, 22.8 mmol) in water (10 mL) was added to a solution of (*Z*)-**19a**[27] (1.16 g, 7.60 mmol) in DMSO (30 mL). The resulting mixture was stirred for 12 h at room temperature, then diluted with

water (50 mL) and extracted three times with diethyl ether. The combined organic layers were washed three times with water, dried with $MgSO_4$, and concentrated in vacuo to give a 1:1 mixture of (*Z*)-**19b** and (*E*)-**19b** (1.04 g, 86%). The geometrical isomers could be separated by flash chromatography ($SiO_2$, hexane/diethyl ether, 9:1); (*Z*)-**19b** was eluted first and was obtained as a light-yellow liquid after workup of the appropriate fraction. − IR ($CDCl_3$): $\tilde{\nu}$ = 2101 $cm^{-1}$ ($N_3$). − $^1H$ NMR ($CDCl_3$): δ = 4.08 (d, $^3J$ = 7 Hz, 3-H), 5.79 (dt, $^3J$ = 11 Hz, $^3J$ = 7 Hz, 2-H), 6.78 (d, $^3J$ = 11 Hz, 1-H), 7.19−7.42 (m, 5 H). − $^{13}C$ NMR ($CDCl_3$): δ = 48.51 (t), 124.64 (d), 127.61 (d), 128.41 (d), 128.70 (d), 133.95 (d), 135.69 (s).

The irreversible rearrangement (*Z*)-**19b** → (*E*)-**19b** was monitored by $^1H$ NMR spectroscopy by heating a sealed tube containing a solution of (*Z*)-**19b** and an internal standard in $CDCl_3$ at 60°C in a thermostat. No by-products nor the postulated intermediate **20** could be detected.

**(*E*)-3-Azido-1,3-diphenylprop-1-ene [(*E*)-21c]:** To a solution of sodium azide (5.00 g, 76.9 mmol) in dry DMSO (150 mL) was added (*E*)-**21d** (10.93 g, 40.0 mmol). The resulting mixture was stirred for 2 d at room temperature, then poured into ice/water (450 g) and extracted three times with pentane. The combined organic layers were washed with water, dried with $MgSO_4$, and concentrated in vacuo to give (*E*)-**21c** (9.13 g, 97%) as a white solid. The $^1H$ NMR spectrum of the product was identical to that reported in ref.[29a], which described an alternative synthesis of (*E*)-**21c**.

**Reaction of 1-Bromo-1*H*-indene (24a) with Sodium Azide:** A solution of sodium azide (2.64 g, 40.6 mmol) in water (16 mL) was added to a solution of **24a**[34] (4.00 g, 20.5 mmol) in methanol (80 mL) and the mixture was stirred for 11 d at ca. 30°C. The methanol was then evaporated in vacuo, and the residue was diluted with water and extracted three times with diethyl ether. The combined organic layers were washed with water, dried with $MgSO_4$, and concentrated in vacuo to yield **25** (2.93 g, 91%). The product could be purified by distillation (**safety shield !**); b.p. 46°C/0.02 Torr. − IR ($CDCl_3$): $\tilde{\nu}$ = 2120 $cm^{-1}$ ($N_3$). − $^1H$ NMR ($CDCl_3$): δ = 3.43 (d, $^3J$ = 2.5 Hz, 1-H), 6.05 (t, $^3J$ = 2.5 Hz, 2-H), 7.2−7.5 (m, 4 H). − $^{13}C$ NMR ($CDCl_3$): δ = 35.77 (t), 114.85 (d), 118.27 (d), 123.83 (d), 125.68 (d), 126.21 (d), 139.17 (s), 140.57 (s), 143.07 (s). The NMR spectra of the product were identical to those of **25** synthesized by another method.[8]

When **24a** was similarly treated with sodium azide in aqueous methanol, but for 1 h at 20°C instead of 11 d at ca. 30°C, analogous workup furnished **24b** (95%) as a light-yellow liquid. The product could be recondensed at 20°C/0.001 Torr. On attempted distillation (b.p. 50°C/0.02 Torr) it partially isomerized to **25**. − IR ($CCl_4$): $\tilde{\nu}$ = 2100 $cm^{-1}$ ($N_3$). − $^1H$ NMR ($CDCl_3$): δ = 4.73 (s, br., 1-H), 6.38 (dd, $^3J$ = 6 Hz, $^3J$ = 2 Hz, 2-H), 6.88 (br. d, $^3J$ = 6 Hz, 3-H), 7.2−7.6 (m, 4 H). − $^{13}C$ NMR ($CDCl_3$): δ = 65.96 (d), 121.58 (d), 123.49 (d), 126.14 (d), 128.64 (d), 133.08 (d), 134.39 (d), 141.62 (s), 142.69 (s).

**(*Z*)-1-Azido-1,3-diphenylprop-1-ene [(*Z*)-26] from (*E*)-21c:** To a solution of sodium hydroxide (3.64 g, 91.0 mmol) in methanol (225 mL) was added (*E*)-**21c** (5.00 g, 21.3 mmol). The resulting mixture was stirred for 4 d at ca. 30°C, then diluted with ice/water (150 g) and extracted three times with diethyl ether. The combined organic layers were washed with 5% $H_2SO_4$ and with saturated aqueous $NaHCO_3$ solution, dried with $MgSO_4$, and concentrated in vacuo to afford (*Z*)-**26** (2.85 g, 57%) as a yellow oil. − IR ($CDCl_3$): $\tilde{\nu}$ = 2110 $cm^{-1}$ ($N_3$). − $^1H$ NMR ($CDCl_3$): δ = 3.60 (d, $^3J$ = 7.4 Hz, 3-H), 5.35 (t, $^3J$ = 7.4 Hz, 2-H), 7.2−7.4 (m, 10 H). − $^{13}C$ NMR ($CDCl_3$): δ = 33.26 (t, *J* = 128.5 Hz), 118.84 (d), 126.05 (d), 126.94 (d), 128.30 (d), 128.44 (d), 128.57 (d), 128.67 (d), 134.81 (s), 137.21 (s), 140.12 (s).

The $^1H$ NMR spectrum of the product was identical to that of (*Z*)-**26** and significantly different from that of (*E*)-**26**, both synthesized by another method.[36] Since our $^1H$ NMR data of (*E*)-**26** show considerable differences compared to those in ref.[36], our spectrum of (*E*)-**26** is also given: $^1H$ NMR ($CDCl_3$): δ = 3.42 (d, $^3J$ = 7.9 Hz, 3-H), 5.59 (t, $^3J$ = 7.9 Hz, 2-H), 7.1−7.5 (m, Ph).

**(*Z*)-1-Azido-1,3-diphenylprop-1-ene [(*Z*)-26] from 22:** A solution of **22**[33] (100 mg, 0.282 mmol) in dry DMSO (5 mL) was added to a solution of sodium azide (80 mg, 1.2 mmol) in dry DMSO (5 mL). The mixture was stirred for 2.5 d at room temperature, then diluted with water and extracted repeatedly with diethyl ether. The combined organic layers were washed three times with water, dried with $MgSO_4$, and concentrated to give (*Z*)-**26** (67 mg, ca. 100%) as a yellow oil. The $^1H$ NMR spectrum of the crude product showed only small amounts of impurities, most probably 1-bromo-1,3-diphenylprop-1-ene and traces of (*E*)-**21c**. When the reaction was performed in [$D_6$]DMSO and monitored by $^1H$ NMR spectroscopy, no significant amounts of (*E*)-**21c** but rather transient substitution products of **22** could be observed.

**2-Benzyl-3-phenyl-2*H*-azirine (27):** A solution of (*Z*)-**26** (2.00 g, 8.50 mmol) in $CHCl_3$ (50 mL) was stirred for 2 d at 60°C. After removal of the solvent in vacuo, the remaining yellow oil (1.34 g) was purified by chromatography ($SiO_2$, pentane/diethyl ether, 9:1) to give **27** (890 mg, 51%) as a light-yellow oil. − IR ($CCl_4$): $\tilde{\nu}$ = 1732 $cm^{-1}$ (C=N). − $^1H$ NMR ($CDCl_3$): δ = 2.45 (t, $^3J$ = 5.2 Hz, 2-H), 2.70 (dd, $^2J$ = 14.6 Hz, $^3J$ = 5.2 Hz, 1 H), 2.99 (dd, $^2J$ = 14.6 Hz, $^3J$ = 5.1 Hz, 1 H), 7.15−7.75 (m, 10 H). − $^{13}C$ NMR ($CDCl_3$): δ = 33.09 (d, *J* = 180 Hz, C-2), 40.06 (t, *J* = 129 Hz), 125.39, 126.19, 128.41, 128.81, 128.90, 129.25, 132.69, 139.24, 171.47 (s, C-3). − MS (70 eV); *m/z* (%): 207 (24) [$M^+$], 206 (84), 104 (100). − MS (HR-EI): 207.10479 ($C_{15}H_{13}N$: calcd. 207.10480).

The transformation (*Z*)-**26** → **27** could also be achieved by photolysis using a high-pressure mercury lamp.

**Photolysis of 3-Azidoprop-1-enes in the Presence of Acetophenone:** A solution of (*E*)-**19b** (30 mg, 0.19 mmol) and acetophenone (7 μL, 0.06 mmol) in [$D_6$]benzene (1 mL) was irradiated at 0°C using a high-pressure mercury lamp. The maximum yield of the isomerization product was reached after a reaction time of 6 h, i.e. 22% (*Z*)-**19b** along with 41% of the starting material (*E*)-**19b** ($^1H$ NMR). Prolonged photolysis (11.5 h) led to 19% (*Z*)-**19b** and 19% (*E*)-**19b**.

The photolysis of (*E*)-**21c** was performed analogously at −30°C using a solution in [$D_8$]toluene. After an irradiation time of 1.5 h, 11% (*Z*)-**21c** besides 52% (*E*)-**21c** were found ($^1H$ NMR).

On similar irradiation of an equilibrium mixture of (*E*)-**3** and (*Z*)-**3**, photochemical decomposition but no significant change in the ratio of the azides could be observed.

**Reaction of 3 with Strong Bases:** A solution of **3** (160 mg, 0.51 mmol) in dry benzene (5 mL) was added dropwise to a solution of [$(Me_2N)_3P{=}N]_3P{=}NtBu$ (phosphazene base $P_4$-*t*Bu, Fluka; 32 mg, 0.050 mmol) in dry benzene/hexane, 100:1 (5 mL). The resulting mixture was stirred for 60 min at room temperature, and then filtered through silica gel eluting with diethyl ether. Concentration of the eluate in vacuo gave (*E*)-**28** (130 mg, 89%) as a yellow oil. − $^{13}C$ NMR ($CDCl_3$): δ = 127.99, 128.09, 128.17, 128.55, 129.02, 129.67, 129.83, 129.91, 135.32 (s), 136.66, 139.33 (s), 140.72 (s), 179.46 (s, C=NH). Obviously, the $^{13}C$ NMR signals could not be resolved completely.

When (*E*)-**28** was stirred in dioxane/5% $H_2SO_4$, 2:1, for 2 d at room temperature, workup gave mainly (*E*)-**29**. − $^{13}C$ NMR ($CDCl_3$):

δ = 127.77, 128.08, 128.12, 128.62, 128.80, 129.48, 129.62, 130.17, 132.01, 134.56 (s), 136.30 (s), 137.96 (s), 140.09, 140.54 (s), 197.41 (s, C=O). The $^{13}$C NMR spectrum of the product was identical to that of (*E*)-**29** synthesized by another method.[37]

On treatment of **3** with KO*t*Bu in *tert*-butyl alcohol (16 h/30°C) followed by hydrolysis, similar results were obtained.

When **3** was reacted with $CD_3ONa$ in $CD_3OD$ (12 h/60°C), NMR monitoring indicated that almost half of the starting material had been consumed. However, no incorporation of deuterium into the recovered **3** could be detected.

**Reaction of Azides with Cyclooctyne:** Solutions of the azides (*E*)-**4**, (*Z*)-**4**, (*E*)-**26**, and (*Z*)-**26** in diethyl ether or chloroform were treated with a three- to eightfold excess of cyclooctyne. In the case of **26**, the azides were transformed within a few minutes at room temperature to furnish (*Z*)-**26t** (98% yield) or (*E*)-**26t** (75% after flash chromatography on silica gel eluting with diethyl ether/hexane, 3:1). The azides **4** were allowed to react with cyclooctyne for a few hours. Small-scale preparations were performed in NMR tubes, which gave high yields of triazoles, e.g. 96% (*E*)-**4t**, 84% (*Z*)-**4t**. Cooling might be necessary for syntheses on a larger scale.

The crude mixture of products obtained from *unlike*-**7** (329 mg, 1.00 mmol), pyridine, and thionyl chloride, as described above was taken up in diethyl ether (5 mL). This solution was stirred at 0°C and treated with cyclooctyne (868 mg, 8.02 mmol). After 2.5 h at room temperature, all volatile components were removed in vacuo. The resulting triazoles could be separated by HPLC {LiChrospher Si 60 (5 μm), 2 cm Ø × 20 cm, ethyl acetate/hexane, 1:3, flow rate 5 mL/min, $t_R$ [(*E*)-**4t**] = 4.5 min, $t_R$ [(*Z*)-**4t**] = 8.1 min] to afford 60 mg (14% based on *unlike*-**7**) of (*E*)-**4t** and 60 mg (14%) of (*Z*)-**4t**.

**(*E*)-1-(1,2,3-Triphenylprop-1-enyl)-4,5,6,7,8,9-hexahydro-1*H*-cyclooctatriazole [(*E*)-4t]:** Colorless solid, m.p. 175−177°C. − $^1$H NMR ($CDCl_3$): δ = 1.32 (m, 2 H), 1.75 (t, br., 2 H), 2.41 (t, *J* = 6 Hz, 9-H), 2.91 (t, *J* = 6.4 Hz, 4-H), 3.63 (s, 3′-H), 6.88−7.19 (m, 15 H). − $^{13}$C NMR ($CDCl_3$): δ = 21.79 (t), 24.38 (t), 25.06 (t), 25.56 (t), 25.76 (t), 27.86 (t), 40.67 (t, C-3′), 126.20 (d), 127.66 (d), 127.92 (d), 127.97 (d), 128.12 (d), 128.27 (d), 129.21 (d), 129.22 (d), 129.43 (d), 132.13 (s), 134.48 (s), 136.15 (s), 137.48 (s), 138.86 (s), 143.07 (s), 144.56 (s). − $C_{29}H_{29}N_3$ (419.6): calcd. C 83.02, H 6.97, N 10.02; found C 82.87, H 7.05, N 9.83.

**(*Z*)-1-(1,2,3-Triphenylprop-1-enyl)-4,5,6,7,8,9-hexahydro-1*H*-cyclooctatriazole [(*Z*)-4t]:** Colorless solid, m.p. 152−153°C. − $^1$H NMR ($CDCl_3$): δ = 1.41 (quint, *J* = 6.2 Hz, 2 H), 1.60 (quint, br., *J* = 5.8 Hz, 2 H), 2.54 (t, br., *J* = 6 Hz, 9-H), 2.78 (t, *J* = 6.5 Hz, 4-H), 4.15 (s, 3′-H), 7.08−7.40 (m, 15 H). − $^{13}$C NMR ($CDCl_3$): δ = 22.31 (t), 24.09 (t), 24.35 (t), 25.57 (t), 25.86 (t), 27.49 (t), 39.89 (t, C-3′), 126.32 (d), 127.68 (d), 128.00 (d), 128.07 (d), 128.47 (d), 128.48 (d), 128.57 (d), 128.67 (d), 128.86 (d), 133.03 (s), 134.30 (s), 136.17 (s), 137.92 (s), 138.02 (s), 141.39 (s), 143.59 (s). − $C_{29}H_{29}N_3$ (419.6): calcd. C 83.02, H 6.97, N 10.02; found C 82.69, H 6.65, N 9.97.

**(*E*)-1-(1,3-Diphenylprop-1-enyl)-4,5,6,7,8,9-hexahydro-1*H*-cyclooctatriazole [(*E*)-26t]:** Light-yellow oil. − $^1$H NMR ($CDCl_3$): δ = 1.34 (m, 6 H), 1.74 (m, 2 H), 2.47 (m, 9-H), 2.89 (m, 4-H), 3.76 (d, $^3J$ = 8.0 Hz, 3′-H), 6.31 (t, $^3J$ = 8.0 Hz, 2′-H), 7.16−7.41 (m, 10 H). − $^{13}$C NMR ($CDCl_3$): δ = 21.95 (t), 24.47 (t), 25.08 (t), 25.55 (t), 26.14 (t), 28.18 (t), 34.25 (t), 126.54 (d), 128.20 (d), 128.29 (d), 128.66 (d), 128.74 (d), 129.03 (d), 129.91 (d), 133.91 (s), 134.26 (s), 135.96 (s), 138.94 (s), 144.81 (s). − $C_{23}H_{25}N_3$ (343.5): calcd. C 80.43, H 7.34, N 12.23; found C 80.20, H 7.45, N 12.16.

**(*Z*)-1-(1,3-Diphenylprop-1-enyl)-4,5,6,7,8,9-hexahydro-1*H*-cyclooctatriazole [(*Z*)-26t]:** Light-yellow oil. − $^1$H NMR ($CDCl_3$): δ = 1.46 (m, 6 H), 1.82 (m, 2 H), 2.51 (m, 9-H), 2.99 (m, 4-H), 3.29 (d, $^3J$ = 7.6 Hz, 3′-H), 6.62 (t, $^3J$ = 7.6 Hz, 2′-H), 7.07−7.33 (m, 10 H). − $^{13}$C NMR ($CDCl_3$): δ = 21.65 (t), 24.47 (t), 25.08 (t), 25.75 (t), 26.18 (t), 27.97 (t), 34.14 (t), 125.06 (d), 126.54 (d), 128.59 (d), 128.66 (d), 128.73 (d), 128.78 (d), 129.74 (d), 134.59 (s), 135.29 (s), 135.82 (s), 138.47 (s), 144.67 (s). − $C_{23}H_{25}N_3$ (343.5): calcd. C 80.43, H 7.34, N 12.23; found C 79.96, H 7.35, N 12.10.

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