(M^+ – 63). Anal. Calcd for $C_{25}H_{24}NOCl$: C, 77.12; H, 6.17; N, 3.6. Found: C, 77.06; H, 6.21; N, 3.45.

2-(1-Chloropropyl)-5-ethyl-2,4,6-triphenyl-5,6-dihydro-2*H*-1,3-oxazine (5b): major epimer ^1H NMR ($CDCl_3$, 80 MHz) δ_H 0.4 (t, 3 H, J = 7.1 Hz), 1.0 (t, 3 H, J = 7.0 Hz), 1.7 (m, 4 H), 2.8 (m, 1 H), 4.2 (dd, 2 H, J = 8.0 Hz), 4.8 (d, 1 H, J = 3.0 Hz), 7.1–8.0 (m, 15 H); minor epimer[17] ^1H NMR ($CDCl_3$, 300 MHz δ_H 4.9 (d, 1 H, J = 3.0 Hz); ^{13}C NMR ($CDCl_3$, 20 MHz) δ_C 168.96, 143.36, 140.8, 138.88, 131.2–125.44, 94.08, 71.68, 70.4, 40.32, 24.32, 19.84, 12.8, 10.24; MS, m/z 417 (M^+). Anal. Calcd for $C_{27}H_{28}N_8OCl$: C, 77.70; H, 6.71; N, 3.36. Found: C, 77.58; H, 6.8; N, 3.4.

2-(1-Chloroethyl)-2,4-diphenyl-6-(1-phenylethyl)-5,6-dihydro-5-methyl-2*H*-1,3-oxazine (5c): major epimer ^1H NMR ($CDCl_3$, 300 MHz) δ_H 1.1 (d, 3 H, J = 7.0 Hz), 1.26 (d, 3 H, J = 6.7 Hz), 1.40 (d, 3 H, J = 6.7 Hz), 2.37 (dq, 1 H, J = 2.5 and 7.0 Hz), 2.95 (m, 1 H), 3.53 (dd, 1 H, J = 2.5 and 10.5 Hz), 4.39 (q, 1 H, J = 6.7 Hz), 6.8–7.9 (m, 15 H); minor epimer[17] ^1H NMR ($CDCl_3$, 300 MHz) δ_H 1.03 (d, 3 H, J = 7.0 Hz), 3.72 (d, 1 H, J = 2.5 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ_C 168.72, 143.28, 142.35, 137.06, 130.16–126.46, 94.11, 74.30, 65.01, 41.39, 31.17, 20.90, 20.54, 11.87; MS, m/z 354 (M^+ – 63). Anal. Calcd for $C_{27}H_{28}NOCl$: C, 77.70; H, 6.71; N, 3.36. Found: C, 77.48; H, 6.8; N, 3.44.

2-(1-Chloroethyl)-6-phenyl-5,6-dihydro-5-methyl-2,4-bis(4-methylphenyl)-2*H*-1,3-oxazine (5d): major epimer ^1H NMR ($CDCl_3$, 300 MHz) δ_H 0.95 (d, 3 H, J = 7.0 Hz), 1.56 (d, 3 H, J = 6.7 Hz), 2.3 (s, 3 H), 2.4 (s, 3 H), 3.02 (m, 1 H), 4.49 (q, 1 H, J = 6.7 Hz), 4.74 (d, 1 H, J = 2.5 Hz), 7.0–7.9 (m, 13 H); minor epimer[17] ^1H NMR ($CDCl_3$, 300 MHz) δ_H 2.38 (s, 3 H), 4.52 (q, 1 H, J = 6.7 Hz), 4.85 (d, 1 H, J = 2.5 Hz); ^{13}C NMR ($CDCl_3$, 20 MHz) δ_C 172.16, 170.24, 144.8–144.0, 137.6, 133.12–128.0, 96.0, 73.6, 72.96, 67.2, 65.56, 35.84, 35.20, 22.4, 21.76, 21.12, 19.84, 13.44, 12.80; MS, m/z 354 (M^+ – 63). Anal. Calcd for $C_{27}H_{28}NOCl$: C, 77.70; H, 6.71; N, 3.36. Found: C, 77.53; H, 6.81; N, 3.40.

2-(1-Chloroethyl)-2,4-diphenyl-5,6-dihydro-5-methyl-6-(4-nitrophenyl)-2*H*-1,3-oxazine (5e): major epimer ^1H NMR ($CDCl_3$, 300 MHz) δ_H 0.97 (d, 3 H, J = 6.8 Hz), 1.57 (d, 3 H, J = 6.7 Hz), 3.12 (m, 1 H), 4.55 (q, 1 H, J = 6.7 Hz), 4.82 (d, 1 H, J = 2.5 Hz), 7.2–8.3 (m, 14 H); minor epimer[17] ^1H NMR ($CDCl_3$, 300 MHz) δ_H 4.95 (d, 1 H, J = 2.5 Hz); ^{13}C NMR ($CDCl_3$, 20 MHz) δ_C 169.6, 167.68, 148.48, 147.84, 147.2, 142.72, 141.44, 137.6, 131.2–126.08, 124.16, 94.08, 70.4, 69.76, 64.64, 33.28, 32.64, 19.2, 18.56, 11.52; MS, m/z 371 (M^+ – 63). Anal. Calcd for $C_{25}H_{23}N_2O_3Cl$: C, 69.12; H, 5.30; N, 6.45. Found: C, 69.01; H, 5.20; N, 6.42.

Crystal Data for 4a. A colorless triclinic crystal (0.40 × 0.36 × 0.33 mm) from chloroform saturated with hexane had space group symmetry of $P\bar{1}$ and cell constants of a = 8.9372 (1) Å, b = 10.1995 (1) Å, c = 13.2285 (1) Å, α = 87.515 (1)°, β = 82.716 (1)°, γ = 83.383 (1)°, V = 1187.13 (5) Å^3, Z = 2, and ρ(calcd) = 1.28 Mg m^{-3}; λ = 0.71073 Å; μ(Mo Kα) = 1.91 cm^{-1}; T = 293 K; 7200 reflections measured on an Enraf-Nonius CAD4 instrument (ω–2θ scan technique), range $0 < \theta < 30$ and $-12 < h < 12$, $-14 < k < 14$, $0 < l < 18$, 6920 unique reflections (R_{int} = 0.018, averaging some double measured) and 4000 observed ($I > 3\sigma(I)$). Semiempirical and empirical absorption corrections were applied. The structure was solved by direct methods, using the program SHELX86, and we anisotropically refined (SHELX76) all non-hydrogen atoms, except for C25, which was found in two disordered positions, namely C25 and C25′, with refined occupation factors of 0.575 (7) and 0.425 (7), respectively, to R = 0.062 and R_w = 0.071 (299 parameters). Maximum shift/error = 0.60 ρ_{max} = 0.41 e/Å^3.

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Supplementary Material Available: List of fractional positional and thermal parameters, bond lengths and angles, anisotropic temperature factors, fractional positional parameters of the hydrogen atoms, bond lengths and angles involving hydrogen atoms, angles between least-squares planes, and principal torsion angles for **4a** (15 pages); observed and calculated structure factors for **4a** (29 pages). Ordering information is given on any current masthead page.

Aryl Azide–Allene Cycloaddition. The Contrasting Behavior of Two Simple Allenes, 1,2-Cyclononadiene and 1,2-Propadiene

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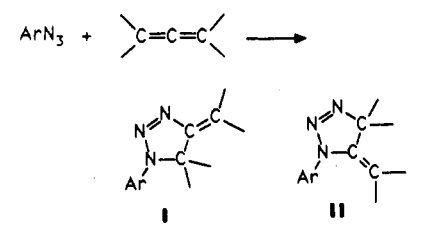
1,2-Cyclononadiene (**1**) reacts with phenyl azide (**2a**) and 4-bromophenyl azide (**2b**) to give conjugated triazoline adducts **3a** and **3b**, respectively. (*R*)-(+)-**1** and **2a** react to give (*S*)-(+)-**3a**, which is consistent with a concerted cycloaddition mechanism. The reaction of 1,2-propadiene (**6**) and **2a** gives triazoles **8** and **10** plus compound **18** in nearly equal amounts. The formation of these products is rationalized by a scheme involving initial formation of triazolines **7** and **9**. Triazoline **3a** is slowly isomerized by sodium ethoxide or *N*,*N*-dimethylaniline to triazole **20**.

The mechanism of the addition of aryl azides to simple alkenes has been extensively studied.[1] The relative insensitivity of the reaction to changes in solvent polarity, the stereospecificity of the addition, the large negative entropy of this kinetically second-order process, and the enhancement of the reaction rate by electron-withdrawing substituents on the aryl azide are consistent with a concerted formation of the 1,2,3-Δ^2-triazoline adduct by way of an unsymmetrical transition state in which the nitrogen

Scheme I



α to the aromatic ring is negative relative to the alkene carbon to which it is bonding. This concerted process is

(1) Huisgen, R. In *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; Wiley: New York, 1984; p 1. Lwowski, W. Ibid. p 559.

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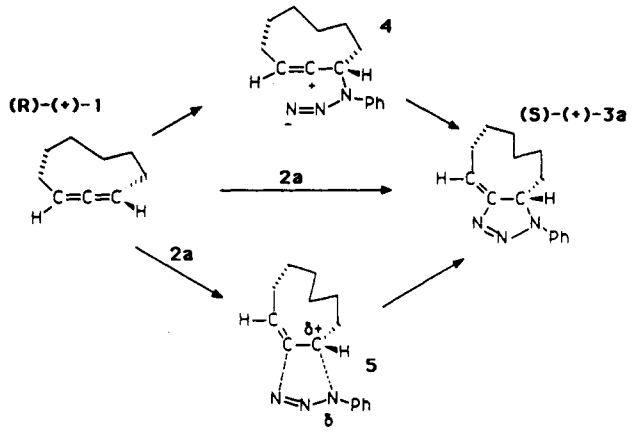
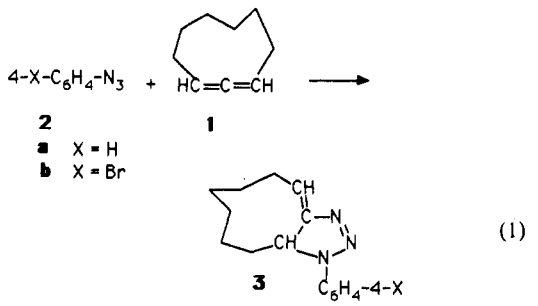
Scheme II



consistent with orbital symmetry considerations.[2]

Although a number of 1,3-dipolar additions to the cumulated double bonds of allenes (1,2-dienes) have been examined, the reaction of azides with allenes has received relatively little attention.[3,4] The straightforward addition of aryl azides to allenes can potentially occur to give regioisomers I and II (Scheme I). When we reacted 1,2-cyclononadiene (1) with phenyl azide (**2a**) or 4-bromophenyl azide (**2b**), 1:1 adducts **3a** or **3b**, respectively, were obtained (eq 1), which are type I structures. The structure

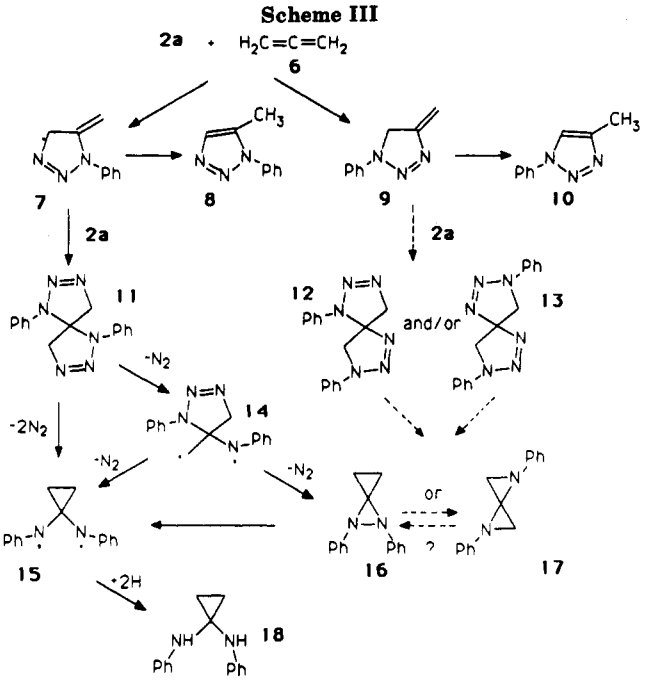


(1)

of **3b** has been determined by X-ray crystallography.[5] The close relationship of the IR, NMR, and UV spectra of **3a** and **3b** establishes the structure assigned to **3a**. The UV spectra of 1-phenyl-1,2,3-Δ^2-triazolines have maxima at 295–320 nm[6] and should be good models for the nonconjugated type II structures. The longer wavelength UV maxima of **3a** (352 nm) and **3b** (355 nm) further support their being type I adducts with both double bonds conjugated.

In order to help elucidate the aryl azide–allene reaction mechanism, optically active 1 ($[\alpha]^{27}_D$ +9.5° (neat); $[\alpha]^{27}_D$ +17.2° corrected for 13% α-pinene from partial resolution of (*R,S*)-1,[7] $[\alpha]^{27}_D$ −42.5°) was reacted with **2a**. The recrystallized adduct, **3a** (no dimer of (+)-1 present by TLC), was obtained optically active, $[\alpha]^{27}_D$ +9.5° (*c* 0.10; $CHCl_3$; average of three experiments). In order to rule out asymmetric induction by α-pinene, excess racemic 1 was reacted with **2a** in the presence of (−)-α-pinene. The adduct, **3a**, showed no optical activity. Therefore, the resultant optical

Scheme III



activity of **3a** is due to the mechanistic consequences of the reaction of (+)-1 with **2a**. This was confirmed by the observation that (−)-1 ($[\alpha]^{24}_D$ −12.7° (*c* 0.03, pentane), GC collected and uncontaminated with α-pinene) reacted with **2a** to give (−)-**3a** ($[\alpha]^{24}_D$ −4.0° (*c* 0.01; pentane)).

The specific rotation of optically pure (+)-1 has been estimated,[8] and it has been determined to have the *R* configuration.[9] Addition of **2a** most certainly occurs preferentially to the least hindered face of either double bond of (*R*)-(+)-1. This predicts that the (+)-**3a** formed has the *S* configuration (Scheme II). By use of the higher estimated value of $[\alpha]^{25}_D$ +175° for enantiomerically pure (*R*)-(+)-1, a minimum value of $[\alpha]^{25}_D$ +97° can be calculated for enantiomerically pure (*S*)-(+)-**3a**, assuming that **2a** adds with 100% stereoselectivity.

A stepwise process in which the terminal azide nitrogen bonds to the central allenic carbon to form either a charge-separated or diradical intermediate of significant lifetime can be ruled out, since the resultant allylic ion or radical system would be achiral and would undergo ring closure to form optically inactive **3a**. A stepwise mechanism involving initial reaction of **2a** with a terminal allenic carbon of (*R*)-(+)-1 by approach from the least hindered side of either double bond to give chiral intermediate **4** (or the analogous diradical), which would subsequently ring close to (*S*)-(+)-**3a**, is consistent with the observed retention of optical activity. However, formation of the relatively unstable vinyl carbocation (or vinyl radical)[10] is not very attractive. Also, nucleophiles add to the terminal nitrogen of **2a** rather than the nitrogen attached to the benzene ring.[11] A more likely interpretation of these results is that **2a** reacts by a concerted mechanism, approaching either double bond from the least hindered direction to give (*S*)-(+)-**3a**. This interpretation agrees with the extensive data that has established the analogous aryl azide–alkene addition as a concerted reaction as well

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as orbital symmetry considerations. Transition state 5, with partial charge separation as indicated, is consistent with the effect of aryl azide substituents on the reaction of aryl azides with simple alkenes as well as the rate-enhancing effect of electron-withdrawing substituents on aryl azides in their reaction with tetramethylallene.[12]

When 2a and excess 1,2-propadiene (6) were reacted at 50, 70, or 100 °C, neither of the straightforward regioisomeric 1:1 adducts 7 or 9 (Scheme III) was obtained. Evidence for these compounds was sought by examination of the vinyl proton region of the NMR spectrum of the crude reaction mixture. No peaks potentially assignable to vinyl proton signals of 7 or 9 were discernible. Instead, three compounds were isolated from this reaction. Two triazoles, 5-methyl-1-phenyl-1,2,3-triazole (8) and 4-methyl-1-phenyl-1,2,3-triazole (10), were obtained. Their formation can be understood in terms of the initial formation of 7 and 9, respectively, followed by isomerization to the more stable aromatic triazole systems. A third compound, 1,1-dianilinocyclopropane (18), was also obtained. Possible pathways to account for the production of 18 involve initial formation of the 1:1 adducts 7 and 9 (Scheme III). There is then a competition between isomerization of 8 and 10, respectively, and addition of a second 2a molecule to give potential intermediates 11, 12, and/or 13. The stepwise decomposition of 11 with loss of a nitrogen molecule giving diradical 14 followed by the loss of a second nitrogen molecule could give diradical 15 directly or indirectly by way of either bis(ethyleneimine) 17 or bicyclic hydrazo compound 16. Diradical 15 must then abstract two hydrogen atoms from the reaction medium to give product 18. The hydrogen atom source has not been established, but a prime candidate is 6, which would give the resonance-stabilized propargyl radical[13] upon loss of a hydrogen atom. Other potential hydrogen atom sources are the "benzylic" methyl hydrogens of 8 and 10 (also xylene when substituted for benzene as the solvent).

In an analogous manner, 12 and 13 could decompose with a stepwise loss of two nitrogen molecules to give diradical 15, which would ultimately be converted to 18. The greatly enhanced carbon–carbon double-bond reactivity of enamines toward 2a[14] implies that the reaction of 2a with enamine adduct 7 will be favored over its reaction with adduct 9. The polar, resonance contribution of the enamine nitrogen to the concerted addition transition state dictates the regiochemistry shown for 11 rather than the opposite regiochemistry, which would result in formation of 12. Thus, the most likely pathway for the formation of 18 involves the sequential conversions of 7 to 11 to 15 (possibly by way of 16 or 17) to 18. Even though the amine nitrogen of 9 is conjugated through the nitrogen–nitrogen double bond to the carbon–carbon double bond, its lower reactivity than 7 toward 2a is consistent with the 2 + 1 reaction results. Only regioisomer 3, which is structurally analogous to 9, is isolated, and we have no evidence of any product resulting from reaction of two 2a molecules with 1, in spite of the fact that the 2a to allene ratio is much higher in the experiments with 1 than with 6.

The formation of 18 by a pathway that involves loss of nitrogen from 7 or 9 to give *N*-phenylalleneimine, which subsequently adds 2a to its carbon–carbon double bond, ultimately giving 18, is extremely unlikely since reaction of *N*-isopropylalleneimine with 2a is reported to give 1-phenyl-5-[(*N*-isopropylamino)methyl]-1,2,3-triazole as the major product.[15] *N*-Isopropyl-*N'*-phenyl-β-lactimide is a minor product. No product analogous to 18 is obtained. Also, the fact that 3 does not readily lose nitrogen at 110 °C is further evidence against a pathway involving nitrogen loss from 7 or 9.

Only very small amounts of purified 8 and 10 were isolated. Compound 18 was isolated in 10% yield (18% yield of slightly less pure material). The ^{1}H NMR spectrum of the crude reaction mixture shows only three singlets between δ 1–3, which are due to each of the three isolated products. By comparing the area of the four cyclopropyl protons (δ 1.2) of 18 with the weighted areas for the methyl protons of 8 (δ 2.38) and 10 (δ 2.42), the minimum yields of triazoles 8 and 10 are each calculated to be 13%. Therefore, these three products account for at least 36% of the fate of 2a. This implies that the rates of formation of initial adducts 7 and 9 are comparable, with 7 probably being formed about twice as fast since it is most likely the precursor of 18 as well as 8, with 9 giving only 10. The preference for 6 to form a nonconjugated type II triazoline adduct (7) by reaction with 2a, in comparison with 1 in which only the conjugated type I triazoline adduct (3a) is found, is consistent with positive charge accommodation in a concerted, charge-separated transition state. In the pathway leading to a type I conjugated adduct, partial positive charge is accommodated on a terminal allenic carbon (no allylic carbocation resonance due to orthogonality of the orbital on the positive carbon with the carbon–carbon double bond). Thus, transition state 5 from 2a reacting with 1, in which the partial positive charge is on a secondary carbon, is relatively more favorable than the analogous transition state from the reaction of 2a with 6, in which the positive charge is on a primary carbon. This diminished stability of the transition state leading to 9 allows the transition state leading to 7, in which partial positive charge is on the central allenic carbon, to become competitive.

The possibility that all or some of the 2a + 6 reaction products are the result of 6 initially isomerizing to 2-propyne (19), which subsequently reacts with 2a, was

$$CH_3-C\equiv C-H$$

19

considered unlikely, since in the absence of catalysts, 6 is stable with respect to isomerization to 19 up to 400 °C.[16] No effective isomerization catalyst appears to be present in the 2a + 6 reactions. Reaction product 18 is the best candidate for an isomerization catalyst, although it is expected to be rather poor due to its weak basicity. In order to completely dismiss the possibility that 6 is being isomerized to 19 in these reactions, a series of control experiments were carried out using the K_2HgI_4 reagent[17] to detect small amounts of 19 (25 ppm detectability limit for 19). When the reaction of excess 6 with 2a was carried out in the usual manner, no 19 was detected. The 18 formed in this reaction is weakly basic and, though unlikely, might have isomerized 6 to 19, which went undetected because it reacted with 2a much faster then did 6. Therefore, *N*-methylaniline (similar basicity to 18) was substituted for 2a in the reaction with 6. Again, no 19 was detected. Since the 6:19 equilibrium ratio is approximately 14:86 at

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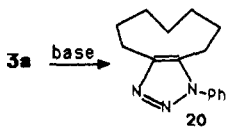
125 °C,[16] clearly 19 can be ruled out as an intermediate in the 2a + 6 reaction.

When 19 is reacted with 2a, the NMR spectrum of the crude reaction mixture reveals the absence of a δ 1.2 resonance characteristic of 18. Absorptions characteristic of 8 and 10 are seen (δ 2.37 and 2.42, respectively) and are about equal. Triazole 10 was isolated in 46% yield. However, 8 could not be isolated. Instead, an impure material having physical and chemical properties different than 8 was obtained. Its NMR spectrum does show a singlet at δ 2.37 and it has not been completely characterized.[18]

In the reaction of 2a with 1, the initial adduct 3a is stable under the reaction conditions and can be isolated, presumably at least in part because no base such as 18 is present or formed that can isomerize it to triazole 20. The isomerization of 3a to 20 (eq 2) was readily carried out with



(2)

sodium ethoxide. Since 18 is the base most likely responsible for isomerizing adducts 7 and 9 to their respectively triazoles, 8 and 10, the effect of the analogous weak base, *N*-methylaniline, on the 3a to 20 isomerization was examined. TLC gave evidence for the formation of some 20 as well as unreacted 3a. Thus, 3a is isomerized to 20, but apparently not nearly as readily as adducts 7 and 9 are converted to triazoles 8 and 10, respectively.

Experimental Section

General. All reactions were carried out under nitrogen, and melting points are corrected. ^{1}H NMR spectra were obtained at 100 MHz using $CDCl_3$ as solvent.

10-Phenyl-10,11,12-triaza-Δ^{11}-bicyclo[7.3.0]dodec-1-ene (3a). A solution of 1[19] (1.22 g, 0.010 mol) and 2a[20] (1.19 g, 0.010 mol) in 15 mL of toluene was refluxed for 10 h. The viscous yellow oil, obtained upon solvent evaporation, crystallized when stored at room temperature for several days. Recrystallization from petroleum ether (60–110 °C) gave 0.51 g (21%) of 3a, mp 90–94 °C, which exhibited a single TLC (silica gel) spot using different solvents: IR (KBr) 2900, 1600 cm^{-1}; ^{1}H NMR δ 0.9–2.7 (m, 12 H), 4.3–4.7 (m, 1 H), 6.02–6.43 (m, 1 H), 6.85–7.7 (m, 5 H); UV (C_2H_5OH) λ_{max} 352 nm (ϵ_{max} 1.2 × 10^4); MS *m/z* 242 (M^+ + 1, 6), 241 (M^+, 49), 213 ($M^+ - N_2$, 17), 156 (100), 119 ($M^+ - C_9H_6$, 26). The material submitted for elemental analysis (mp 91–96 °C) was twice sublimed at 93 °C (0.1 mm). Anal. Calcd for $C_{15}H_{19}N_3$: C, 74.65; H, 7.93; N, 17.41. Found: C, 74.46; H, 8.22; N, 17.31.

10-(4-Bromophenyl)-10,11,12-triaza-Δ^{11}-bicyclo[7.3.0]dodec-1-ene (3b). This reaction is identical with the 3a synthesis except that 2b is used in place of 2a. Recrystallization from methanol gave yellow crystalline 3b (mp 115–117 °C, 28%): IR (KBr) 2900, 1600 cm^{-1}; ^{1}H NMR δ 1.0–2.9 (m, 12 H), 4.3–4.7 (m, 1 H), 6.04–6.53 (m, 1 H), 7.05–7.65 (m, 4 H); UV (C_2H_5OH) λ_{max} 355 nm (ϵ_{max} 1.5 × 10^4); MS *m/z* 322 (^{81}Br M^+ + 1, 4), 321 (^{81}Br M^+, 18), 320 (^{79}Br M^+ + 1, 4), 319 (^{79}Br M^+, 19), 293 (^{81}Br $M^+ - N_2$, 31), 291 (^{79}Br $M^+ - N_2$, 31), 236 (100), 234 (90), 199 (^{81}Br $M^+ - C_9H_{14}$, 23), 197 (^{79}Br $M^+ - C_9H_{14}$, 35). Anal. Calcd for $C_{15}H_{18}N_3Br$: C, 56.3; H, 5.7; N, 13.1; Br, 24.9. Found: C, 56.27; H, 5.77; N, 13.28; Br, 24.90.

(*S*)-(+)-3a. A solution of 1.22 g (8.7 mmol corrected for 13% α-pinene impurity) of (*R*)-(+)-1,[7] $[\alpha]^{27}_D$ +9.5° (neat) ($[\alpha]^{27}_D$ +17.2° corrected for GC determined 13% impurity of α-pinene, $[\alpha]^{27}_D$ −42.5°) and 1.0 g (8.0 mmol) of 2a in 15 mL of toluene was refluxed for 10 h. Evaporation of the solvent gave a viscous yellow oil that crystallized upon standing for 2–3 d at room temperature. Recrystallization from petroleum ether (60–110 °C) gave 0.520 g (24%) of (*S*)-(+)-3a, $[\alpha]^{27}_D$ +9.7° (*c* 0.10; $CHCl_3$), mp 90–94 °C. TLC showed the absence of the dimer of (*R*)-(+)-1 (1% could be detected). Two other identical runs gave (*S*)-(+)-3a, $[\alpha]^{27}_D$ +9.5° (23% yield) and $[\alpha]^{27}_D$ +9.4° (23% yield). With use of (*S*)-(−)-1, $[\alpha]^{27}_D$ −15.3° (neat), uncorrected for α-pinene, reaction with 2a gave (*R*)-(−)-3a, $[\alpha]^{27}_D$ −8.5° (*c* 0.1; $CHCl_3$). With use of GC collected (*S*)-(−)-1, $[\alpha]^{24}_D$ −12.7° (*c* 0.03; pentane), reaction with 2a gave *R*-(−)-3a, $[\alpha]^{24}_D$ −4.0° (*c* 0.01, pentane).

Reaction of 2a with Racemic 1 in the Presence of (−)-α-Pinene. A solution of (*R,S*)-1 (2.0 g, 16 mmol), 2a (1.19 g, 10.0 mmol), and α-pinene (1.0 g, 7.0 mmol), $[a]^{27}_D$ −42.5° (neat, 83% optical purity), in 15 mL of toluene was refluxed for 10 h. The yellow oil, obtained after solvent evaporation, crystallized after standing for several days at room temperature. Recrystallization from petroleum ether (80–110 °C) gave 3a (0.590 g, 37%), mp 90–95 °C, $[\alpha]^{27}_D$ 0.00°.

Isomerization of 3a to 1-Phenyl-4,5-heptamethylene-1,2,3-triazole (20). (i) With Sodium Ethoxide in Ethanol. In order to establish isomerization conditions, (−)-3a (66 mg, 0.27 mmol), $[\alpha]^{27}_D$ −2.4° (*c* 0.006; C_2H_5OH), in 20 mL of 0.5 M sodium ethoxide in ethanol was refluxed overnight. After filtration to remove turbidity, the rotation was $[\alpha]^{25}_D$ −1.0° (*c* 0.003; C_2H_5OH). After 3 d of additional reflux, the reaction mixture did not rotate polarized light. The following scaled-up reaction is based on these preliminary results. A solution of 3a (1.00 g, 4.14 mmol) in 40 mL of 0.75 M sodium ethoxide in ethanol was refluxed for 3 days. After solvent evaporation, the residue was extracted with ether, and the ether extract was washed with water until the aqueous washes were neutral. The ether layer was dried ($MgSO_4$) and evaporated to give 0.81 g of crude product that showed some OH and CO IR absorption. Petroleum ether was added and evaporated (repeated three times), and a brown crystalline solid formed upon standing. Recrystallization from petroleum ether–benzene (3:1) afforded 0.701 g (70%) of white crystalline 20, mp 77–78 °C. UV (C_2H_5OH) λ_{max} 211 nm (ϵ_{max} 1.24 × 10^4); MS *m/z* 241 (M^+, 3.4), 213 (32.2), 77 (100); ^{1}H NMR δ 1.2–2.0 (m, 10 H), 2.7 (m, 2 H), 2.9 (m, 2 H), 7.5–7.8 (m, 5 H). Anal. Calcd for $C_{15}H_{19}N_3$: C, 74.69; H, 7.93; N, 17.42. Found: C, 74.56; H, 7.83; N, 17.33.

(ii) With *N*-Methylaniline. A 76-mg (0.32 mmol) portion of (−)-3a in 10 mL of *N*-methylaniline was heated (108 °C) for 8 d. The solution darkened, making it impossible to follow the progress of the isomerization by polarimetry. Pentane was added, and the organic phase was extracted thoroughly with 5% HCl, then with water, and dried ($MgSO_4$). Evaporation of the solvent left a brown viscous residue that was dissolved in 1 mL of $CHCl_3$. Silica gel TLC (benzene) gave three spots. The major spot had the same R_f (0.83) as 20. One of the smaller spots (R_f = 0.32) corresponded to 3a, and the other minor spot (R_f = 0.89) was not identified.

Reaction of Phenyl Azide (2a) with 1,2-Propadiene (6). An autoclave, equipped with a pressure gauge, a gas inlet, and an outlet, containing 2a (4.0 g, 0.034 mol) and 15 mL of benzene at −40 °C was charged with 8 g (0.2 mol) of 6 (previously condensed at −78 °C) and sealed. It was placed in an oil bath at 100 + 5 °C for 3 weeks. After the reaction mixture was cooled to room temperature, the gas was bubbled through a K_2HgI_4 terminal acetylenic test reagent solution[17] at 0 °C. No precipitate formed (50 μL of 19 mixed with 2 L of nitrogen, 25 ppm, approximately 10^{-6} M of gaseous 19, gave a precipitate). Evaporation of the solvent gave 5.8 g of a brown mixture that was separated by silica gel column chromatography. The first two fractions were eluted with benzene, and subsequent fractions were eluted with ether:benzene (3:1).

The second fraction yielded 0.68 g (18%) of pale yellow 18, mp 140–142 °C. Recrystallization from petroleum ether (30–60 °C) gave white, fluffy crystals (0.39 g, 10%), mp 142–143 °C. Silica gel TLC showed one spot with a tail. A 100-mg sample submitted to silica gel thick-layer chromatography (benzene eluant) gave 45 mg of a white solid, which upon recrystallization from petroleum ether (30–60 °C) gave needles of 18, mp 143–144.5 °C (lit.[21]

(18) Analogous results are obtained from the reaction of ethylacetylene with 2a.

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mp 144-144.5 °C): IR (KBr) 3400 cm^{-1} (NH); ^1H NMR δ 1.2 (s, 4 H), 4.95 (br s, 2 H, disappeared upon addition of D_2O), 6.64-6.88 (m, 6 H), 7.15-7.3 (m, 4 H); MS m/z 225 ($M^+ + 1$, 2.44), 224 (M^+, 14.5), 132 ($M^+ - C_6H_5NH$, 100). Anal. Calcd for $C_{15}H_{16}N_2$: MW, 224; C, 80.35; H, 7.14; N, 12.50. Found: MW by vapor-pressure osmometry, 220; C, 80.25; H, 7.30; N, 12.42.

The third fraction gave 2 g of an oil that was extracted (10 × 25 mL) with boiling petroleum ether (30-60 °C). Cooling the combined extracts to -10 °C for 2 d gave **10** (53 mg, 1%), mp 79-80 °C. Recrystallization from petroleum ether (30-60 °C) gave white crystalline **10**, mp 80-81 °C (lit.[14] mp 80-81 °C): IR (KBr) 3150, 3050, 2920, 1600 cm^{-1}; NMR δ 2.42 (s, 3 H), 7.4-7.8 (m, 6 H); UV (C_2H_5OH) λ_{max} 250 nm (ϵ 0.97 × 10^4); MS m/z 159 (M^+, 3), 131 ($M^+ - N_2$, 53), 77 (100). An authentic sample[14] gave IR and NMR spectra, TLC behavior, and a mixed mp that were identical.

The combined fourth and fifth fractions gave a dark, brown oil (2.3 g) that was extracted (10 × 25 mL) with petroleum ether (30-60 °C). The cooled (-10 °C) extracts yielded 32 mg (0.6%) of **8**, mp 60-62 °C. It was recrystallized from petroleum ether (30-60 °C), mp 62-63.5 °C (lit.[22] mp 64 °C): IR (KBr) 3100, 1600 cm^{-1}; NMR δ 2.38 (s, 3 H), 7.35 (s, 1 H), 7.5-7.65 (m, 5 H); UV (C_2H_5OH) λ_{max} 223 nm (ϵ 1.4 × 10^4). An authentic sample[22] gave IR and NMR spectra, TLC behavior, and a mixed mp that were identical.

When **2a** (4.0 g, 0.034 mol), 20 mL of benzene, and **6** (4 g, 0.1 mol) were heated at 100 °C for 1 week and the gas phase (2.4 L at 25 °C) was passed through the K_2HgI_4 reagent, no precipitate was observed. The reaction was also carried out in sealed, heavy-wall Pyrex tubes using xylene in place of benzene at 100 °C for 1 week, 70 °C for times ranging from 1 to 3 weeks, and at 50 °C for 2 weeks. Similar results were obtained from all reactions (e.g., the TLC and NMR of the crude reaction product mixtures were virtually identical). Since **6** was sometimes passed over NaOH pellets before use in a reaction, it was tested by passing through the K_2HgI_4 reagent both before and after NaOH exposure. No precipitate was observed in either case.

Heating 6 with *N*-Methylaniline. *N*-Methylaniline (3.64 g, 0.034 mol), benzene (15 mL), and **6** (8 g, 0.2 mol) were heated in an autoclave at 105 + 5 °C for 7 d. After being cooled to room temperature, the gas was passed through the K_2HgI_4 reagent (no precipitate formed) and collected (4.0 L at room temperature).

Reaction of 2a with Methylacetylene (19). In an autoclave, **2a** (4.0 g, 0.034 mol), benzene (20 mL), and condensed (-78 °C) **19** (10 g, 0.25 mol) were combined and heated at 100 + 2 °C for 3 d. A dark brown oil was obtained (5.6 g) that showed no IR band for phenyl azide (2130 cm^{-1}). The ^1H NMR exhibited sharp singlets at δ 2.37 and 2.42 as well as resonance in the aromatic region. No resonance at δ 1.2 (**18**) was detected. Silica gel TLC showed two spots and a silica gel column chromatographic separation was undertaken. The first fraction gave 2.46 g (46%) of a white solid, mp 78-80 °C. Recrystallization from petroleum ether (30-60 °C) yielded colorless crystalline **10** (1.8 g, 34%), mp 80-81 °C. The IR, NMR, UV, TLC, mp, and mixed mp of this and an authentic sample[14] of **10** were identical.

The second fraction yielded 3.0 g of a viscous liquid that was short-path distilled and the major fraction collected at 125 °C (2 mm). This material solidified at -10 °C but remained liquid at room temperature: IR (neat) 3450, 3100, 2900, 1600 cm^{-1}; NMR δ 2.37 (s, 3 H), 7.3 (m, 6 H), 7.7 (m, 4 H), 8.08 (s, 1 H). Addition of D_2O to the NMR sample did not effect the spectrum. The elemental analysis gave a high nitrogen value (27.76%). The TLC behavior and the NMR singlet at δ 2.37 are the same as for **8** but the IR is quite different. All attempts to obtain **8** from this material were unsuccessful. A repetition of this experiment produced the same results.

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Asymmetric Reactions of Thioacetals and Their *S*-Oxides Derived from 1,1'-Binaphthalene-2,2'-dithiol[1]

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The chiral dithiepine **3** was selectively oxidized to all possible oxides: the sulfoxide **9**, the sulfone **16**, the sulfone-sulfoxide **20**, the disulfoxide **21**, and the disulfone **22**. The sulfinyl oxygens of **9**, **14**, **20**, and **21** are always in the pseudoaxial configuration, as shown by the X-ray structure determination of **11a**. Reaction of the anions of **3**, **9**, and **16** with methyl iodide, benzaldehyde, or acetophenone occurs efficiently. The stereoselectivity of the processes is high and maximized in sulfoxide **9**, where the contributions of the chiral binaphthyl residue and the sulfoxide appear to occur synergistically. The alcohols derived from reaction of the anions of **3**, **9**, and **16** with benzaldehyde and acetophenone were also prepared in high yield and stereoselectivity via reduction or methylation of the phenyl ketone **8** and of its oxidized homologues **14** and **19**. Alcohol **6a**, prepared in 8:2 ratio in the reaction of **3** with benzaldehyde, was obtained as a single diastereoisomer in the reduction of **8** with lithium aluminum hydride.

"Umpolung" of the carbonyl group via the thioacetal[4] is a powerful tool for the synthesis of a variety of functionalized molecules. However, asymmetric variants, making use of thioacetals derived from chiral thiols, remain to be explored. Work has been done with related molecules

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