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- Enders*, D., Scherer, H. J., Runsink, J. 1929 ▶ Diastereo- und enantioselektive Synthese 1,2-*trans*-substituierter Cycloalkancarbonsäureester und Sulfone durch Michael-initiierte Cyclisierungen via SAMP-/RAMP-Hydrazone
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- Bott, K. 1955 ▶ Alkylierungsreaktionen mit Alkoholen und Kohlenmonoxid: Eine breit anwendbare Synthese von Thioethern und von Coffein aus Theophyllin
- Bingel, C. 1957 ▶ Cyclopropanierung von Fullerenen

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- Diastereo- and Enantioselective Synthesis of 1,2-*trans*-substituted Cycloalkancarboxylates and Sulfones by Michael-Initiated Cyclisation via SAMP/RAMP Hydrazones
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▶ Relationship between Dominant Conformation and Diastereoselectivity of *O*-Acetal Formation of Saturated 2*H*-3,1-Benzothiazine-2-thiones

Alkylation Reactions by Means of Alcohols and Carbon Monoxide: An Efficient Synthesis of Thioethers and of Caffeine from Theophylline

Cyclopropylation of Fullerenes

▶ Language of Publication

A Stepwise [4 + 3] Cycloaddition Reaction of the 1,3-Diphenyl-2-azaallyl Anion[☆]

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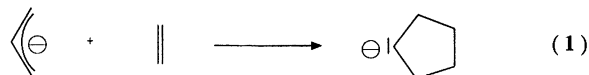
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Key Words: 2-Azaallyl anion, 1,3-diphenyl / [4 + 3] Cycloaddition / Concertedness / Pyrrolidines / Azepine, tetrahydro-

The 1,3-diphenyl-2-azaallyl anion (**1**) undergoes [3 + 2] cycloaddition reactions with the *s-cis*-fixed 1,3-dienes **8–11**. In contrast, 1,1,2,2,3,3-hexamethyl-4,5-bis(methylene)cyclopentane (**7**) reacts with **1** to give the [4 + 3] cycloadduct **13** and the linear 1,4-addition product **14**. This reaction is four orders of magnitude slower than the corresponding reaction of **1** with

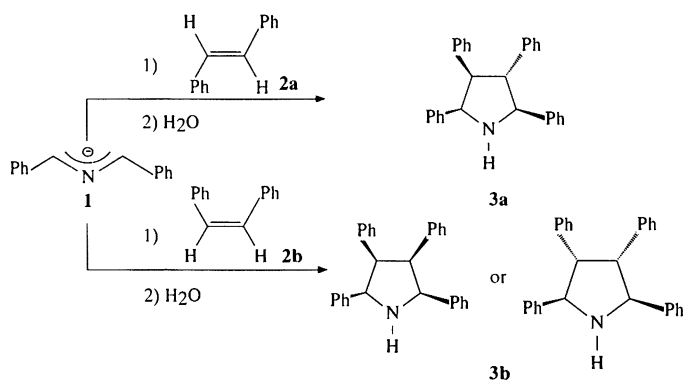
1,2-bis(methylene)cyclopentane (**8**), which exclusively yields [3 + 2] cycloadducts. A change of mechanism – concerted cycloaddition of **8** and stepwise cycloaddition of **7** – is suggested, but not unequivocally proven. It is concluded that reactions of **1** with ordinary dienes cannot profit from concertedness by more than 5 kcal · mol⁻¹.

Cycloadditions of allyl anions to CC double bonds (eq. 1), have been classified as orbital symmetry-allowed [$\pi 4_s + \pi 2_s$] processes by Woodward and Hoffmann^[1].



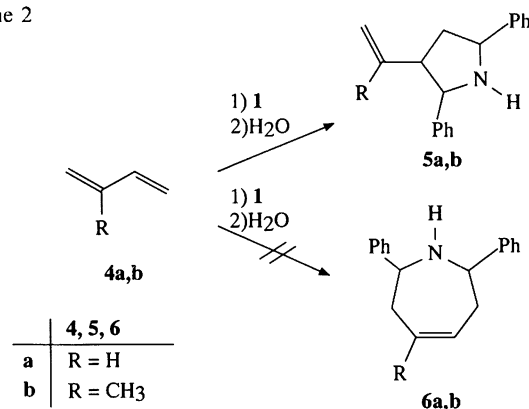
Prior to the experimental realization of this reaction^[2], analogous cycloadditions of 2-azaallyl anions have been reported. In accord with a concerted process, Kauffmann et al. found stereospecific cycloaddition of 1,3-diphenyl-2-azaallyl anion (**1**) to (*E,Z*)-isomeric alkenes with retention of configuration of the alkene and of the azaallyl anion moiety (Scheme 1)^[3]. The mechanistic impact of this observation has been questioned^[4], however, because the isolated yield of cycloadducts was rather low [21% with (*Z*)-stilbene (**2b**)].

Scheme 1



Further evidence for a concerted pathway has been derived from the exclusive formation of vinylpyrrolidines **5** obtained by reaction of **1** with 1,3-butadiene (**4a**) and isoprene (**4b**)^[5]. There is no evidence for the formation of a tetrahydroazepine **6**, which might have been generated by a stepwise pathway since its formation by a concerted cycloaddition reaction is orbital symmetry-forbidden (Scheme 2).

Scheme 2

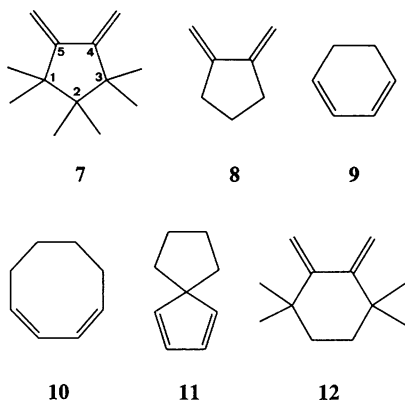


Cycloheptatriene, on the other hand, reacts with 1,1- and 1,3-diphenylazaallyl anion to give exclusively [6 + 3] cycloaddition products^[6], in accord with an orbital symmetry-allowed [$\pi 4_s + \pi 6_s$] process.

Recently, we have demonstrated that the *s-cis*-fixed diene **7** can be used as a probe for the study of cycloaddition mechanisms^[7]. Since the nonterminal positions of the diene fragment of **7** are sterically shielded, 1,4-additions have been observed even with such cycloaddends which generally undergo 1,2-additions with ordinary dienes (carbenes^[7b], ketenes^[7c], nitrones^[7d,e], 1,3-dienes^[7f]^(1,8)). We have now in-

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investigated the reaction of **1** with **7** and other *s-cis*-fixed dienes (**8–12**) and present the first observation of a [4 + 3] cycloaddition product with an azaallyl anion.

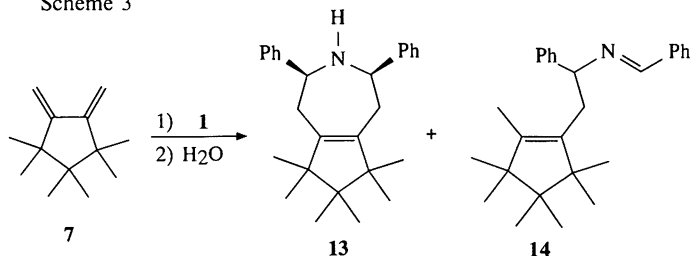


Results

When 1,3-diphenyl-2-azaallyllithium (**1**-Li⁺), prepared from *N*-benzylidenebenzylamine and LDA (1.1 equiv.), was allowed to react with diene **7** in THF for four days at room temperature, the crystalline compound **13** was isolated in 47–52% yield after aqueous workup. The ¹³C-NMR spectrum of **13** shows the presence of four different methyl resonances, in accord with the *cis*-arrangement of the two phenyl groups. Analysis of the mother liquors by GC/MS indicated the presence of five more compounds with M⁺ = 373 (0.5–7% yield).

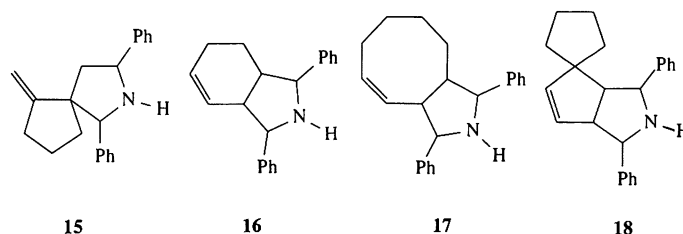
A different reaction course was observed, however, when moisture was not rigorously excluded from the reaction mixture. The yield of the cycloadduct **13** decreased to 10–30% while **14**, one of the side products mentioned above, became the main product (Scheme 3). Up to 36% yield of **14** was isolated, when *N*-benzylidenebenzylamine was deprotonated in a THF solution containing 1.5 equiv. of LDA and 0.3 equiv. of water. The suggested structure of **14** was in accord with the ¹H-NMR signal at δ = 8.18 (1H) and the observation of 7 methyl signals in the ¹³C-NMR spectrum. An interconversion between **13** and **14** by treatment of either compound with LDA under the reaction conditions was not observed.

Scheme 3



Analogous reactions of **1** with the *s-cis*-fixed dienes **8**, **9**, and **10** gave mixtures of products, from which the regular [3 + 2] cycloadducts **15**, **16**, and **17** were isolated in 86, 47, and 41% yield, respectively. The reaction with diene **8** gave a 2:1 mixture of two diastereoisomers of **15**, from which

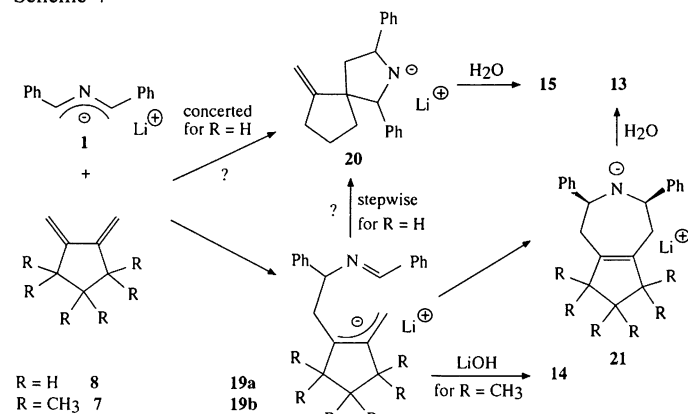
only the main component was isolated in pure form. The stereochemistry of this compound and of **16–18** was not determined. Diene **11** did not react with **1** at room temperature, but upon heating at 65°C the [3 + 2] cycloadduct **18** was produced in 9% yield. We were not able to obtain a reaction product from diene **12**, probably because nonplanarity of the π system (dihedral angle according to MMP 2: 54°) and steric shielding of the methyl groups conjoin to reduce the reactivity of **12**.



Discussion

Compound **7** was the only 1,3-diene investigated, which gave rise to the formation of a [4 + 3] cycloadduct. A stepwise cycloaddition mechanism, as suggested by the orbital symmetry rules, was supported by the isolation of compound **14**, a trapping product of the intermediate **19a** (Scheme 4). As reported above, the formation of compound **14** was only observed, when some water was present in the reaction mixture. Since water is deprotonated by LDA in this solution, we assume that protonation of **19a** takes place within an aggregate of LiOH with **19a**-Li⁺. Diisopropylamine cannot be responsible for the protonation of **19a**, as **14** was not formed in significant amounts, when the reaction of **1** with **7** was carried out in anhydrous THF in the presence of 5 equiv. of HN(*i*Pr)₂.

Scheme 4



The formation of different types of products from the dienes **7** and **8** can be explained in two different ways. Possibly both dienes undergo stepwise cycloadditions via the intermediates **19a, b** (Scheme 4), and cyclization of **19** to a five-membered ring is only possible for R = H. In the case of R = CH₃, steric shielding might inhibit this cyclization resulting in the formation of **13** and/or **14**.

Alternatively, one might assume that **8** undergoes a concerted cycloaddition, which is inhibited by the steric bulkiness of the methyl groups in **7**. Consequently, the diene **7** has to react via **19b**, which is expected to yield products **13** and **14** for the reasons discussed above.

In a previous review^[7a], we have discussed that these two possibilities might be distinguished by kinetic experiments. If both, methylated and nonmethylated diene **7** and **8**, reacted stepwise, similar rates *would* be expected for both reactions, since in the rate-determining step (formation of **19**) the steric effect of the methyl groups is not yet realized^[7a]. On the other hand, if a concerted mechanism was assumed to account for the formation of the [3 + 2] cycloadduct, the steric effect of the methyl groups *would* become effective in the rate-determining step, and **7** should react more slowly than **8**. The different types of products obtained from **7** and **8** would indicate that the methyl groups in **7** raise the barrier for the concerted cycloadditions sufficiently, so that the stepwise mechanism via **19** becomes enforced.

Kinetic investigations of the reaction of **1**-Li⁺ with **7** and **8** in THF at 24.5 °C gave second-order rate constants of $k_2(\mathbf{7}) = (6.08 \pm 0.24) \cdot 10^{-5} \text{ l mol}^{-1} \text{ s}^{-1}$ and $k_2(\mathbf{8}) = (5.1 \pm 0.3) \cdot 10^{-1} \text{ l mol}^{-1} \text{ s}^{-1}$. This reactivity ratio is considerably greater than that for the analogous nitron^[7d,e] or nitrile oxide^[9] cycloadditions suggesting that a change from the concerted (**8**) to the stepwise (**7**) mechanism is taking place. This conclusion is not absolutely sure, however, since the different reaction rates of **7** and **8** may partially be due to the hyperconjugative electron-donating effect of the additional methyl groups in **7**, which might slow down the reactions with anionic reaction partners. Concertedness for the reaction of **1** with **8** can thus not be proven. Since compound **8** can be considered as a typical diene, however, we can conclude that reactions of the azaallyl anion **1** with ordinary dienes cannot profit from concertedness by more than 5 kcal · mol⁻¹, i.e., the observed difference in activation free enthalpies for **7** and **8**.

We thank the *Deutsche Forschungsgemeinschaft* (Ma 673/8-1,2) and the *Fonds der Chemischen Industrie* for financial support.

Experimental

IR: Shimadzu IR-435 spectrometer. — NMR (200 MHz): Varian XL 200 spectrometer, tetramethylsilane as internal standard, CDCl₃ as a solvent. — MS (EI): 70-250E VG spectrometer. — Microanalyses: Ilse Beetz, Microanalytisches Laboratorium, D-8640 Kronach, Germany. — Melting points: uncorrected. — GC analyses: Carlo Erba GC 6000 gas chromatograph equipped with FID. — Preparative MPLC separations: 30 × 2.5-cm columns filled with LiChroprep (RP-18 or Si 60, 15–20-μm particles).

Substrates: Dienes **9** and **10** were commercially available and used freshly distilled. Compounds **7**^[10], **8**^[11], and **11**^[12] were prepared according to literature procedures, and 1,1,4,4-tetramethyl-2,3-bis(methylene)cyclohexane (**12**) was obtained by treatment of 1,2-bis(bromomethyl)-3,3,6,6-tetramethyl-1-cyclohexene^[13] with Mg as described for **7**^[10]. 1,3-Diphenyl-2-azaallyllithium (**1**-Li⁺) was prepared in THF solution by deprotonation of *N*-benzylidenebenzylamine^[14] with LDA according to ref.^[3] Diisopropylamine and THF were freshly distilled over LiAlH₄.

Reaction of 1,3-Diphenyl-2-azaallyl Anion (1) with Diene 7 (Standard Procedure): The reaction was performed in an oven-dried flask under nitrogen at room temp. Diisopropylamine (1.24 g, 12.4 mmol) in 5 ml of THF was added to a 1.6 M solution of BuLi in hexane (7.1 ml, 11.3 mmol). The LDA solution thus obtained was stirred for a few min, and after the addition (2 min) of *N*-benzylidenebenzylamine (2.0 g, 10.25 mmol) in THF (5 ml) the deep purple-red solution of **1** was stirred for 0.5 h. Diene **7** (1.83 g, 10.25 mmol) in 5 ml of THF was subsequently added, and the reaction mixture was stirred at ambient temp. for 4 d. Water was then added, and the mixture was extracted with five 20-ml portions of ether. The combined ether extracts were dried with sodium carbonate, and after removal of the solvents under reduced pressure, methanol was added to the yellow residue. The precipitate was collected by filtration and washed with methanol to give a colorless product which was recrystallized from pentane: **13** (1.70 g, 47%).

8,8,9,9,10,10-Hexamethyl-3,5-diphenyl-4-azabicyclo[5.3.0]dec-1(7)-ene (13): m.p. (pentane) 180.5–181 °C. — IR (KBr): $\tilde{\nu} = 3426 \text{ cm}^{-1}$ (br. NH). — ¹H NMR (CDCl₃): $\delta = 0.78$ (s, 3H, CH₃), 0.80 (s, 6H, 2 CH₃), 0.86 (s, 3H, CH₃), 0.98 (s, 6H, 2 CH₃), 2.00 (br. s, 1H, NH), ABM system with $\nu_A = 2.19$, $\nu_B = 2.55$, $\nu_M = 3.66$, and $J_{AB} = 15.0$, $J_{AM} = 9.8$, $J_{BM} = 3.0$ Hz, further split by long-range couplings (6H, 2,6-H, 3,5-H), 7.26 (m, 10H, arom. H). — ¹³C NMR (CDCl₃): $\delta = 20.96$ (q, CH₃), 22.57 (q, CH₃), 23.58 (q, 2 CH₃), 25.06 (q, 2 CH₃), 36.99 (t, C-2,6), 45.73 (s, C-9), 50.37 (s, C-8,10), 65.15 (d, C-3,5), 126.53 (d), 127.05 (d), 128.44 (d), 141.15 (s), 146.83 (s, C-1,7). — MS (70 eV), *m/z* (%): 373 (12) [M⁺], 195 (100), 194 (93), 91 (11). — C₂₇H₃₅N (373.6): calcd. C 86.81, H 9.44, N 3.75; found C 86.81, H 9.38, N 3.83.

Reaction of Diene 7 with 1 in the Presence of Water: The reaction was carried out according to the general procedure, but with an excess of LDA (LDA: 6.7 mmol; *N*-benzylidenebenzylamine: 1.0 g, 5.1 mmol; **7**: 0.91 g, 5.1 mmol). Moreover, before the addition of benzylidenebenzylamine, water (0.027 g, 1.5 mmol) was injected into the reaction mixture. Compounds **13** and **14** (1:2.5, determined by GC and ¹H-NMR analysis) were formed together with traces of other compounds, and 36% of **14** was isolated by preparative LC (RP18; MeOH). Compound **13** was not eluted under these conditions.

1-(2,4-Diphenyl-3-aza-3-butenyl)-2,3,3,4,4,5,5-heptamethyl-1-cyclopentene (14): viscous oil. — IR (KBr): $\tilde{\nu} = 1644 \text{ cm}^{-1}$ (C=N). — ¹H NMR (CDCl₃): $\delta = 0.69$ (s, 3H, CH₃), 0.75 (s, 3H, CH₃), 0.76 (s, 3H, CH₃), 0.81 (s, 3H, CH₃), 0.92 (s, 3H, CH₃), 0.97 (s, 3H, CH₃), 1.28 (s, 3H, CH₃), ABX system with $\nu_A = 2.45$, $\nu_B = 2.63$, $\nu_X = 4.38$ and $J_{AB} = 13.9$, $J_{AX} = 4.4$, $J_{BX} = 9.4$ Hz (3H, CH₂CHN), 7.24–7.73 (m, 10H, arom. H), 8.18 (s, 1H, N=CH). — ¹³C NMR (CDCl₃): $\delta = 10.71$ (q, CH₃), 20.93 (q, CH₃), 22.69 (q, CH₃), 23.93 (q, CH₃), 24.30 (q, CH₃), 24.85 (q, CH₃), 25.59 (q, CH₃), 35.84 (t, CH₂), 45.66 (s, C-4), 49.59, 50.49 (2 s, C-3,5), 75.58 (d, CH=N), 126.74 (d), 126.94 (d), 128.20 (d), 128.29 (d), 128.41 (d), 130.29 (d), 134.67 (s, C-2), 136.51 (s), 140.46 (s), 145.18 (s, C-1), 158.80 (d, CH=N). — MS (70 eV), *m/z* (%): 373 (7) [M⁺], 195 (34), 194 (100), 106 (21). — C₂₇H₃₅N: calcd. 373.27695, found 373.27664 (MS).

Diene 8 and 1: According to the general procedure (reaction time 1 h), the reaction of **8** (0.0820 g, 0.867 mmol), *N*-benzylidenebenzylamine (0.168 g, 0.858 mmol), and LDA (0.94 mmol) afforded a mixture of two diastereoisomers of **15** (0.213 g, 86% yield) which was separated by preparative LC (RP18; MeOH). The main isomer **15** (32%) was isolated after several LC separations.

6-Methylene-1,3-diphenyl-2-azaspiro[4.4]nonane (15): viscous oil. — ¹H NMR (CDCl₃): $\delta = 0.79$ –1.05 (m, 1H, 9-H), 1.12–1.38 (m, 2H, 8-H), 1.40–1.65 (m, 1H, 9-H), ABX system with $\nu_A = 1.82$,

$\nu_B = 2.43$, $\nu_X = 4.50$ and $J_{AB} = 12.7$, $J_{AX} = 7.6$, $J_{BX} = 8.7$ Hz (3H, 3,4-H), 1.94–2.42 (m, 3H, 7-H, NH), 4.49 (s, 1H, 1-H), 5.11 (br. s, 1H, =CH₂), 5.19 (br. s, 1H, =CH₂), 7.12–7.60 (m, 10H, arom. H). — ¹³C NMR (CDCl₃): $\delta = 22.84$ (t, C-8), 33.67 (t, C-7), 37.80 (t, C-9), 52.01 (t, C-4), 56.31 (s, C-5), 59.14 (d, C-3), 71.21 (d, C-1), 104.81 (t, =CH₂), 126.64 (d), 126.93 (d), 127.42 (d), 127.54 (d), 127.73 (d), 128.26 (d), 141.93 (s), 145.53 (s), 159.80 (s, C-6).

Diene 9 and 1: After a reaction time of 2 d, **9** (1.6 g, 20 mmol), *N*-benzylidenebenzylamine (3.90 g, 20 mmol), and LDA (20.5 mmol) gave **16** which was isolated by crystallization from ether (−15 °C). Recrystallization from hexane/ether (80:20) afforded pure **16** (2.59 g, 47% yield) as colorless needles.

7,9-Diphenyl-8-azabicyclo[4.3.0]non-2-ene (16): m.p. (hexane/ether) 60–62 °C. — ¹H NMR (CDCl₃): $\delta = 1.65$ (mc, 1H, 5-H), 1.75–1.89 (m, 1H, 5-H), 1.96–2.11 (m, 2H, 4-H), 2.14–2.32 (m, 2H, 6-H, NH), 2.57 (m, 1H, 1-H), 3.98 (d, $J_{1,9} = 8.6$ Hz, 1H, 9-H), 4.06 (d, $J_{6,7} = 6.0$ Hz, 1H, 7-H), AB system with $\nu_A = 5.63$, $\nu_B = 5.84$ and $J_{AB} = 10.1$ Hz, further split by allylic, homoallylic and/or long-range couplings, (2H, 2,3-H), 7.25–7.60 (m, 10H, arom. H). — ¹³C NMR (CDCl₃): $\delta = 23.38$, 24.97 (2 t, C-4,5), 45.98, 47.35 (2 d, C-1,6), 66.65, 68.06 (2 d, C-7,9), 126.84 (d), 126.90 (d), 127.00 (d), 127.11 (d), 127.19 (d), 127.89 (d), 128.31 (d, two signals overlapped), 143.88 (s), 145.48 (s). — MS (70 eV), m/z (%): 275 (3) [M⁺], 195 (100), 194 (52), 91 (10). — C₂₀H₂₁N (275.4): calcd. C 87.23, H 7.68, N 5.08; found C 87.08, H 7.59, N 5.33.

Diene 10 and 1: Compounds **10** (0.770 g, 6.66 mmol), *N*-benzylidenebenzylamine (1.30 g, 6.66 mmol), and LDA (8.66 mmol) were allowed to react within 3 d to give crude **17** which was isolated by preparative LC (Si 60; CH₂Cl₂). Crystallization from hexane gave pure **17** (0.83 g, 41% yield) as colorless needles.

9,11-Diphenyl-10-azabicyclo[6.3.0]undec-2-ene (17): m.p. (hexane) 94.5–96 °C. — ¹H NMR (400 MHz, CDCl₃): $\delta = 1.09$ –1.22 (m, 1H, 5-H), 1.23–1.38 (m, 1H, 5-H), 1.40 (mc, 2H, 7-H), 1.73 (mc, 2H, 6-H), 2.05–2.14 (m, 2H, 4-H), 2.16 (mc, 1H, 8-H), 2.35 (br. s, 1H, NH), 3.22 (mc, 1H, 1-H), 3.79 (d, $J_{8,9} = 10.5$ Hz, 1H, 9-H), 4.29 (d, $J_{1,11} = 3.65$ Hz, 1H, 11-H), AB system with $\nu_A = 5.61$, $\nu_B = 5.87$ and $J_{AB} = 10.8$, $J_{1,2} = 11.4$, $J_{3,4} = 7.5$ Hz, 2H, 2,3-H), 7.20–7.60 (m, 10H, arom. H). — ¹³C NMR (CDCl₃): $\delta = 25.07$, 27.94, 28.94, 30.20 (4 t, C-4,5,6,7), 48.79 (d, C-8), 55.29 (d, C-1), 67.81, 68.16 (2 d, C-9,11), 126.58 (d), 126.65 (d), 127.24 (d), 127.63 (d), 128.23 (d), 128.31 (d), 131.90, 133.06 (2 d, C-2,3), 143.35 (s), 146.55 (s). — MS (70 eV), m/z (%): 303 (6) [M⁺], 195 (100), 194 (40), 106 (16), 105 (11), 91 (38). — C₂₂H₂₃N (303.4): calcd. C 87.08, H 8.30, N 4.61; found C 87.35, H 8.34, N 4.31.

Diene 11 and 1: Diene **11** (0.800 g, 6.66 mmol) and **1** obtained from *N*-benzylidenebenzylamine (1.30 g, 6.66 mmol) and LDA (8.66 mmol) were refluxed (7 h). Compound **18** (0.19 g, 9%) was isolated by crystallization from pentane (−60 °C) as colorless crystals.

2,4-Diphenylspiro[3-azabicyclo[3.3.0]oct-7-ene-6,1'-cyclopentane] (18): m.p. (pentane) 56–57 °C. — ¹H NMR (CDCl₃): $\delta = 1.36$ –1.39 (m, 1H), 1.43–1.49 (m, 6H), 1.50–1.70 (m, 1H), 2.10 (br. s, 1H, NH), 2.73 (t, $J_{5,4} = J_{5,1} = 8.9$ Hz, 1H, 5-H), 3.39 (X part of ABX system with $J_{AX} = 2.0$, $J_{BX} = 1.95$, and $J_{5,1} = 8.9$, $J_{2,1} = 6.3$ Hz, 1H, 1-H), 3.98 (d, $J_{2,1} = 6.3$ Hz, 1H, 2-H), 4.08 (d, $J_{5,4} = 8.9$ Hz,

1H, 4-H), AB part of ABX system with $\nu_A = 5.60$, $\nu_B = 5.69$ and $J_{AB} = 5.5$ Hz, 2H, 7,8-H), 7.21–7.55 (m, 10H, arom. H). — ¹³C NMR (CDCl₃): $\delta = 23.39$, 23.82 (2 t, C-3',4'), 32.39, 41.86 (2 t, C-2',5'), 57.95 (s, C-6), 58.92 (d, C-5), 61.04 (d, C-1), 65.77 (d, C-4), 67.83 (d, C-2), 126.65 (d), 126.86 (d), 127.16 (d), 128.25 (d), 128.30 (d), 128.36 (d), 129.74 (d, C-8), 139.06 (d, C-7), 143.55 (s), 144.85 (s). — MS (70 eV), m/z (%): 315 (4) [M⁺], 195 (100), 194 (36), 143 (23), 91 (16). — C₂₃H₂₃N: calcd. 315.1987, found 315.19933 (MS).

Kinetic Measurements: The reactions were carried out with equimolar amounts (1.3 mmol) of **1** and diene (**7** or **8**) in THF (total volume 10 ml) in the presence of 1-phenyldodecane (internal standard) according to the standard procedure. After certain periods, 0.5-ml portions of the solution were taken and the reaction was quenched by injection into a CH₃OH/H₂O solution. Then the samples were analyzed by GC on a fused silica capillary column SE 30 (length 25 m, i.d. 0.2 mm, carrier N₂, $p = 50$ kPa, column temp. 240 °C). Retention times (area factors) for standard, **13**, and **15** were 2.86 (1.0), 20.64 (1.349), and 7.51 (1.489) min, respectively.

* Dedicated to Professor R. W. Hoffmann on the occasion of his 60th birthday.

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