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Stereochemistry of the [2+4] cycloaddition of cyclopentyne

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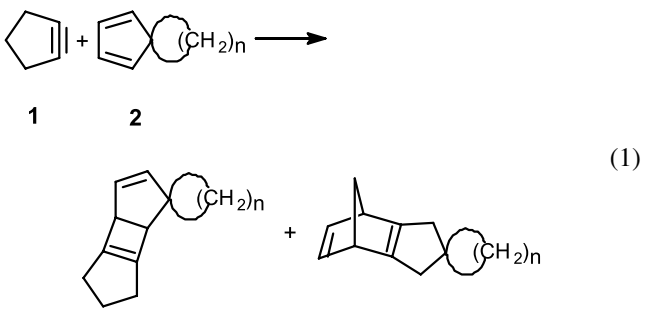
Abstract—The [2+4] cycloaddition of cyclopentyne with a pair of diastereomeric 1,3-dienes is found to occur with high stereoselectivity. The results support the applicability of the principles of orbital symmetry even in the case of this exceedingly reactive dienophile.

1. Introduction

Cyclopentyne (**1**) undergoes both [2+2] and [2+4] cycloaddition reactions with spiro-1,3-cyclopentadienes **2** (n=2, 4) as shown in Eq. 1.[1] Remarkably, the [2+2] process is completely diastereoselective when stereochemically

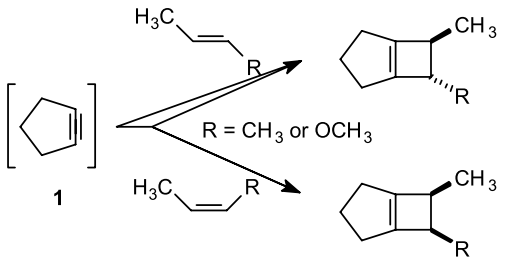


(1)

labeled alkenes are used to trap **1** (Scheme 1).[2] This result, which could be taken as a signal for concert,[3] is inconsistent with the principle of orbital symmetry,[4] and we have recently proposed an alternate mechanism to account for this outcome.[5] The essence of the alternative is that the [2+2] cycloadduct forms by stereospecific ring expansion of a cyclopropylcarbene, itself derived by [2+1] cycloaddition of cyclopentyne to the alkene (Eq. 2).

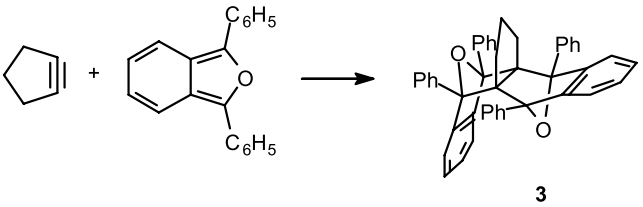
(2)

The [2+4] process has precedent in Wittig's isolation of the double Diels–Alder adduct **3** from reaction of **1** with



Scheme 1.

2,5-diphenylisobenzofuran (Eq. 3).[6] Although this is a thermally-allowed reaction and should be stereospecific,[4] two



(3)

factors stimulated our interest in exploring the Diels–Alder reaction of **1** with a pair of diastereomeric 1,3-dienes capable of stereorandomization in a non-concerted process: (1) the unusual nature of the [2+2] cycloaddition with cyclopentyne and (2) the predicted diradical character of the in-plane π-bond of the cycloalkyne;[7] the latter property could foster a stepwise process leading to stereorandomization (Scheme 2).

Fitjer, et al., had previously reported that reaction of cyclopentyne with 1,3-butadiene afforded the corresponding [2+2] cycloadduct exclusively.[8] We surmised that this was because the diene exists predominantly in its *s-trans* conformation and dictated our probing the stereochemistry of the Diels–Alder reaction of cyclopentyne using a system

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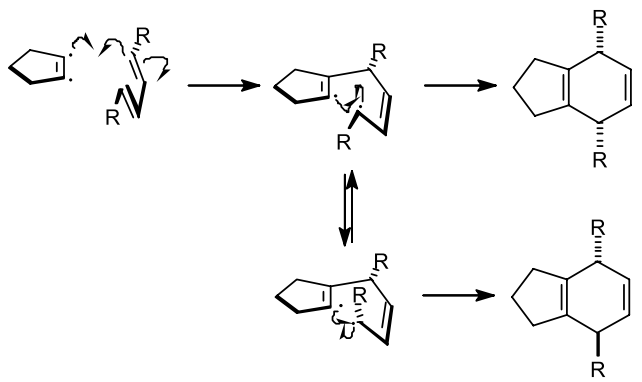
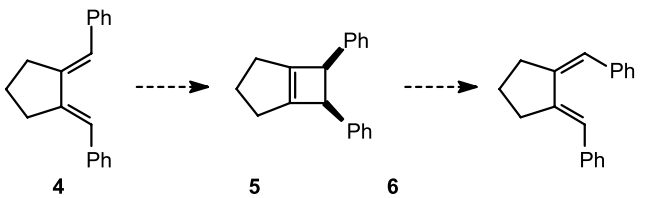


Scheme 2.

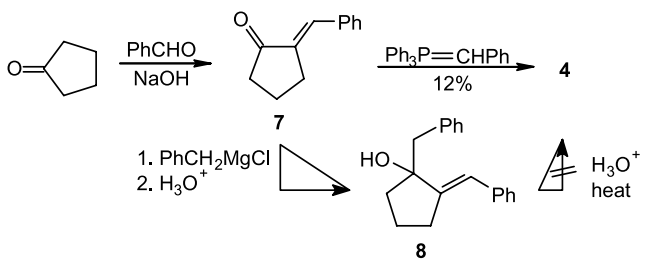
wherein the diene moiety is locked *s-cis*. Dienes **4** and **5** (Eq. 4) were selected for the following reasons: (1) the presence of identical substituents at the termini of the diene simplifies characterization of the cycloadducts; (2) 1,2-dialkylidenecyclopentanes generally react faster in Diels–Alder reactions than do their six-membered ring analogs[9] (3) synthesis of diastereomerically pure **4** had been reported[10]—because the yields of pericyclic reactions involving cyclopentyne and unactivated 1,3-dienes are usually low,[1] contamination of the substrate with a minor amount of a diastereomer could clearly compromise interpretation of the experimental results; (4) although synthesis of **5** had not been reported, we anticipated that it could be prepared by photocyclization of **4**[11] and thermally-induced conrotatory ring-opening of the resulting cyclobutene **6** (Eq. 4).[12]



(4)

2. Synthesis of dienes

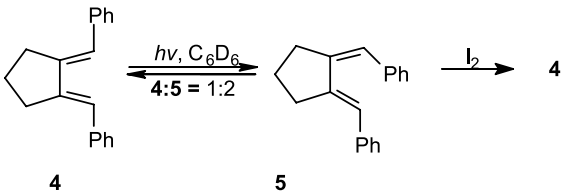
It was reported that (*E*,*E*)-1,2-dibenzylidenecyclopentane (**4**) could be formed from **7**, itself the product of benzylidenation of cyclopentanone, by reaction with either benzylidenetriphenylphosphorane,[10a] or with phenylmagnesium bromide followed by dehydration (Scheme 3).[10b] In our hands, only the Wittig reaction gave the diene, however. Attempted acid-catalyzed dehydration



Scheme 3.

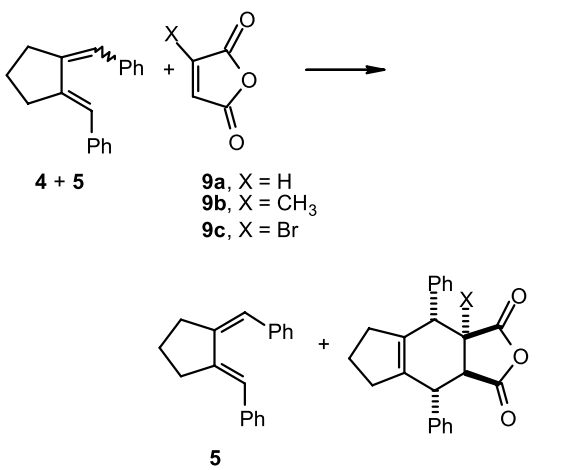
of the alcohol **8** returned only starting alcohol and polymer. As previously reported,[13] **4** was diastereomerically pure.

Turning to our proposed synthesis of the (*E*,*Z*)-diene **5**, irradiation (300–350 nm) transformed **4** into a mixture of **5** and the starting diene. The ^{1}H NMR spectrum of the reaction mixture contained two new vinylic absorptions of equal intensity and three new resonances ascribable to methylene groups. No resonances could be detected for cyclobutene **6**. That the isomer formed by irradiation of **4** was **5** was shown by adding a catalytic amount of molecular iodine to the NMR solution of the two isomers, whereupon quantitative conversion to **4** occurred, as judged from the ^{1}H NMR spectrum (Eq. 5)[†] A photoequilibrium of **4**/**5**=1:2 was established upon prolonged irradiation.



(5)

Because attempts to separate **4** and **5** by column chromatography proved unsuccessful, their kinetic resolution was explored (Eq. 6). Proposed transition states for the Diels–Alder reaction of **4** and **5** with anhydrides **9** are shown in Figure 1. Where the phenyl rings of **4** and **5** coplanar with the diene function, steric interactions with the incoming dienophile should be comparable for both diastereomers and no kinetic resolution would be expected. Such coplanarity, however, is unlikely, given the differing



(6)

steric repulsions expected in the dienes. Distortion from planarity should be particularly prominent for the phenyl group on the *Z* double bond of **5**, hindering approach to the dienophile and thereby increasing the energy of the transition state for the Diels–Alder reaction. Although steric interactions involving the dienophile and the phenyl groups of **4** are likely as well, they should be less important because of decreased distortion from planarity. This isomer should thus react faster than **5** with dienophiles **9**.

To test our assumptions computationally, the geometries of the (*E*,*E*)- and (*E*,*Z*)-dienes were calculated using AM1 and

[†] Iodine is known to promote *cis–trans* isomerization to thermodynamically more stable alkenes or dienes.[14]

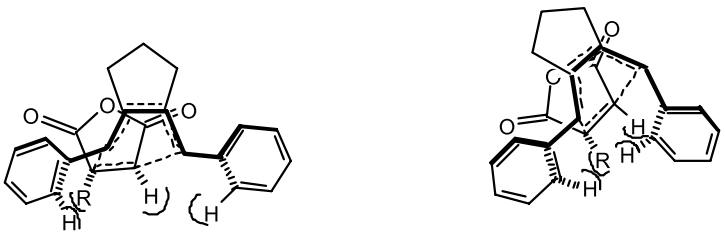


Figure 1. Possible steric effects in Diels–Alder reaction of **4** and **5** with maleic anhydrides **9**.

MM2 methodologies. Table 1 lists the dihedral angle of the phenyl rings relative to the plane of the diene moiety. Both computational approaches predict greater rotation out of the plane for the phenyl ring on the *Z* double bond of **5**. Other calculated properties of the two dienes that might define kinetic selectivity in [2+4] cycloadditions, for example, bond lengths and HOMO/LUMO energies, are very similar to each other. Consequently, the success of a kinetic resolution of **4** and **5** according to Eq. 6 appeared to depend on differing steric environments of the reacting π-systems.

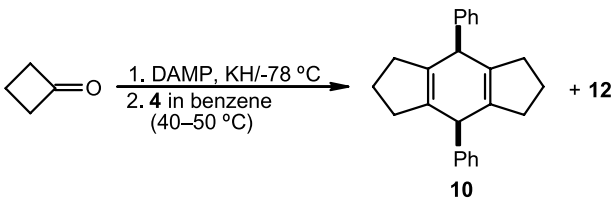
Table 1. Calculated dihedral angles (°) between the diene plane and a phenyl ring

	AM1	MM2
E,*E*-diene **4**	40.9	49.4
E,*Z*-diene **5** (*E*-phenyl)	38.8	50.0
E,*Z*-diene **5** (*Z*-phenyl)	64.2	59.7

In the event, bromomaleic anhydride (**9c**) afforded the best selectivity between **4** and **5** of the three anhydrides evaluated, presumably because the bromo substituent simultaneously increases the steric hindrance and the electrophilicity of dienophile **9c**; **9b**, which also has increased steric hindrance but decreased electrophilicity compared to maleic anhydride itself, is inert toward the two dienes.[15] In practice, treating a 2:1 mixture of **4** and **5** with 0.5 equiv. of **9c** afforded a 1:73 ratio of the two dienes, as determined by integration of the ^{1}H NMR spectrum; thus, (*E*,*Z*)-diene **5** was contaminated with slightly over 1% of the (*E*,*E*) diastereomer.

3. Reactions of cyclopentyne with (*E*,*E*)-diene 4 and (*E*,*Z*)-diene 5

Reaction of **4** with a solution derived by adding cyclobutanone to diethyl diazomethylphosphonate (DAMP)[4] and sodium hydride (Eq. 7), a combination of reagents known to produce cyclopentyne,[2b] afforded two 1:1 adducts of cyclopentyne and **4** in a ratio of 1:1.6.



(7)

Both the ^{1}H and ^{13}C NMR spectra of the earlier-eluting fraction were consistent with its being *cis*-4,8-diphenyl-1,2,3,4,5,6,7,8-octahydro-*s*-indacene (**10**). Definitive proof of the structure was obtained through X-ray crystallography, and an ORTEP plot is provided in Figure 2. The *cis* relationship of the phenyl rings was defined by the existence of a two-fold rotation axis of symmetry perpendicular to and through the center of the cyclohexadiene ring (Fig. 2a). This stereochemical relationship is seen in Figure 2b. The C2–C6 and C2′–C6′ bond distance is 1.33 Å, typical for a carbon–carbon double bond, and the C1–C2–C6–C1′ dihedral angle is 1.9°, showing that the cyclohexadiene ring is essentially planar.

The second isomer formed in the reaction (Eq. 7) had a more complicated ^{1}H NMR spectrum than **10**, possessing among

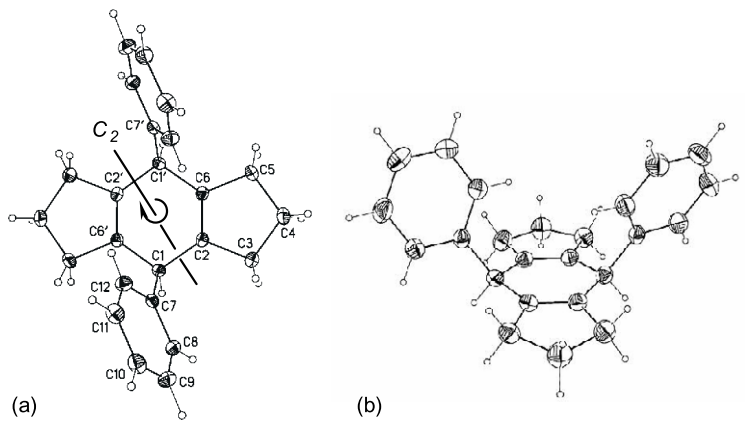
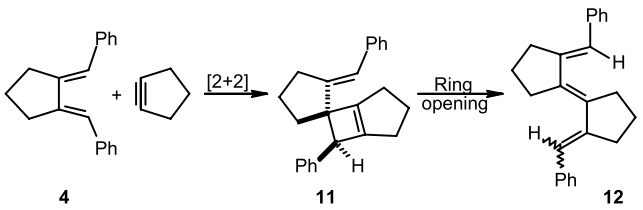


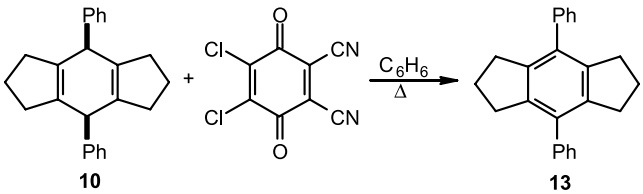
Figure 2. ORTEP plot of cycloadduct **10**: (a) top view and (b) edge view.

other absorptions four vinylic resonances in the range, δ 4.4–6.9 ppm. Although the lability of this product precluded its isolation, the NMR data are consistent with its being a diastereomer of the triene **12**, which could be derived from thermally promoted conrotatory ring-opening of the [2+2] cycloadduct **11** (Eq. 8). That the product was not the *trans* isomer of **10** is clear from the NMR analysis, however. Assuming our tentative structural assignment of **12** is correct and that it arises from **11**, the ratio of [2+2]:[2+4] cycloaddition in the reaction of **4** with cyclopentyne is 1:1.6.‡



(8)

Treating **10** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) fostered aromatization to **13** in 75% isolated yield (Eq. 9).[16] This product was characterized spectroscopically and provided NMR and MS data entirely consistent with the structural assignment. Formation of **13** was useful for the subsequent analysis of the products from reaction of (*E*,*Z*)-diene **5** with cyclopentyne (vide infra).

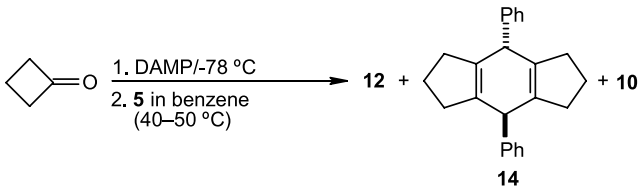


(9)

The result obtained from the reaction of cyclopentyne (**1**) with (*E*,*E*)-diene **4** (Eq. 7) demonstrates that the [2+4] cycloaddition is stereospecific. Such an outcome is entirely consistent with the transformation being concerted, despite the unusual nature of the π system of **1** that is involved in the cycloaddition.

Extending the study of the stereochemistry of the Diels–Alder reaction to (*E*,*Z*)-diene **5** was complicated by various factors. Two isomers having the proper value of *m*/*z* for a 1:1 adduct of **1** and **5** were formed. One had a GC retention time identical to that of the product **12** derived from [2+2] cycloaddition and was assigned as such (Eq. 10), whereas the second was tentatively assigned as the [2+4] cycloadduct **14**. Its retention time was less than that of **10**, as shown by GC analysis of the reaction mixture spiked with authentic **10**.§ Unfortunately, the low yield (3–5%) of this isomer and the presence of impurities generated by treating the reaction mixture with maleic anhydride to remove excess (*E*,*Z*)-diene **5** prevented purification. Diene **5** has a lower reactivity toward maleic anhydride as compared to **4**, and this meant that a longer reaction time was required to remove the excess of it; consequently undesired reactions of the diene, for example, oligomerization and isomerization, apparently occurred. The similarity in R_f value of the cycloadduct and its contaminants, their presence in relatively large amounts, and its low yield made isolation of the cycloadduct impossible.

These difficulties necessitated using an indirect method to characterize the presumed [2+4] cycloadduct. Treating the reaction mixture with DDQ effected aromatization to **13**. Interpretation of this experimental result, however, was complicated by the fact that the starting (*E*,*Z*)-diene **5** was contaminated slightly over 1% of the *E*,*E*-isomer **4**, so that reaction of this contaminant would produce **10**; this in turn would afford **13** upon treatment of the reaction mixture with DDQ. Indeed, careful examination by GC of the crude reaction mixture obtained from the Diels–Alder reaction of **5** with cyclopentyne (Eq. 10) revealed a peak having a retention time identical to that of **10**. Fortunately, the area of this peak was only 3–4% of that assigned as *trans*-cycloadduct **14**, whereas the amount of terphenyl **13** produced by oxidation of the reaction mixture was 17–22% of that of the original **14**.¶ This proves that the majority of the **13** formed arose from an isomer different from **10** and is consistent with this isomer being **14**. Thus, although the structure of **14** has not been proven unambiguously, we firmly believe it to be the *trans* isomer.



(10)

It might be argued that the formation of **10** in a yield greater than of percentage (~1%) of diene **4** that contaminants **5** represents diastereomerization during the course of the [2+4] cycloaddition of **5**. However, knowing that **4** reacts much faster with dienophiles (vide supra) than does **5**, we ascribe the increase in yield of **10** to this kinetic factor and believe that **5** reacts in a concerted fashion in the [2+4] cycloaddition as does **4**.

4. Conclusion

The stereochemistry of the Diels–Alder reaction of cyclopentyne with the (*E*,*E*)-diene **4** afforded cycloadduct **12** stereospecifically within experimental error; less than 2% of the diastereomer **14** relative to **10** could have been detected had it been formed. The result with the (*E*,*Z*)-diene **5** is less definitive because of contamination with **4**, but a 'worst-case scenario' would make the [2+4] cycloaddition in this case greater than 95% stereoselective with retention. Given the enhanced reactivity of **4** relative to **5**

‡ The fact that [2+4] cycloaddition is favored over the [2+2] analog is consistent with our previous observations for the reaction of cyclopentyne with 1,3-cyclopentadienes.[1]

§ The shorter retention time of **14** relative to **10** on GC columns is also consistent with the *trans* structure. The lower yield of oxidation product, relative to that obtained from **10**, may be associated with the known[16] slower rate of oxidation of *trans*-3,6-disubstituted-1,3-cyclohexadienes as compared to the *cis*-isomers.

¶ These percentages are based on the GC integrations in which two impurities that are unreactive toward DDQ served as internal standards.

in the Diels–Alder reaction, however, we believe this cycloaddition to be stereospecific as well. Consequently, it can be concluded that the stereocontrol associated with the principle of orbital symmetry[4] still applies, despite the abnormal characteristics associated with the in-plane π-bond of cyclopentyne.

5. Experimental

5.1. General

All reactions were performed under an atmosphere of dry N_2 in flamed-dried one-neck flasks equipped for magnetic stirring. Low-temperature baths of −40 °C were obtained with an immersion cooler using acetone as the bath liquid. Ice/water, dry ice/acetone and isooctane/$N_{2(l)}$ were used for 0, −78 and −107 °C baths, respectively. Commercially available chemicals were used without further purification unless noted otherwise. Solvents were dried and distilled under an inert atmosphere before use. Et_2O and THF were distilled from sodium benzophenone ketyl, CH_2Cl_2 from CaH_2, and diisopropylamine from KOH. Solutions were concentrated by rotary evaporation at water aspirator pressures.

Quantitative GC analyses were obtained with an analytical gas chromatograph interfaced with an recording integrator and equipped with a 25 m×0.25 mm AT-1 (100% dimethylpolysiloxane) capillary column and a flame-ionization detector; the carrier gas was helium (1.2 mL/min). GC/MS analyses were performed using a 12 m×0.22 mm GB-5 (95% dimethyl-, 5% diphenylpolysiloxane) capillary column with helium as the carrier gas (1.0 mL/min) and interfaced with an electron impact ion trap detector mass spectrometer. High-resolution MS analyses were obtained using the EI mode (70 eV).

^{1}H NMR spectra were obtained at 250 MHz, unless otherwise noted, and ^{13}C NMR spectra were measured at 125 MHz. All chemical shifts are referenced to the solvent, which was $CDCl_3$ unless otherwise noted.

5.1.1. (*E*,*Z*)-1,2-Dibenzylidenecyclopentane (5). A solution of *E*,*E*-1,2-dibenzylidenecyclopentane[11] (1.02 g, 4.14 mmol) in benzene (35 mL) in a 100-mL Pyrex flask equipped with a septum was exposed to UV light (Hanovia 450-W lamp) for 11 h, after which the solution was filtered to remove precipitates and concentrated. The residual oil (0.65 g) was combined with $CHCl_3$ (11 mL), and $NaHCO_3$ (100 mg, 1.2 mmol) in a 50-mL flask. This solution was cooled to 0 °C, bromomaleic anhydride (233 mg, 1.32 mmol) was added, and the mixture was stirred for 18 h. Filtration, concentration, and chromatography over silica gel using ethyl acetate–hexane (1:19) as eluant afforded **5** (R_f=0.58, 303 mg, 1.23 mmol, 30%) as a colorless oil.

Spectral data. ^{1}H NMR (500 MHz): δ 1.81 (2H, m), 2.53 (2H, m), 2.76 (2H, m) 6.48 (1H, s) 6.76 (1H, s); ^{13}C NMR (C_6D_6): δ 24.2, 33.3, 36.0, 119.0, 123.4, 125.8, 126,.0, 127.7, 128–129 (4C), 138.8, 139.2, 140.7, 144.0; HRMS *m*/*z* calcd for C_9H_{18} 246.1409, found 246.1401.

5.1.2. Isomerization of (*E*,*Z*)-1,2-dibenzylidenecyclopentane (5) to (*E*,*E*)-1,2-dibenzylidenecyclopentane (4). A solution of diene **4** (20 mg) in C_6D_6 (1 mL) in an NMR tube was exposed to UV light for 1 h. The ^{1}H NMR spectrum of the resulting solution indicated formation of a 1:1 mixture of the dienes **4** and **5**. Iodine (2 mg) was added and the resulting dark brown solution was immediately analyzed by ^{1}H NMR spectroscopy; only resonances of the diene **4** were observed.

5.1.3. *cis*-4,8-Diphenyl-1,2,3,4,5,6,7,8-octahydro-*s*-indacene (10). Potassium hydride (657 mg, 5.75 mmol, 35% in mineral oil) in a 50-mL flask was washed with pentane (3×10 mL). Dry CH_2Cl_2 (1.5 mL) was added, the slurry was cooled to −78 °C, and a solution of diethyl (diazomethyl)-phosphonate (DAMP)[17] (760 mg, 4.27 mmol) in CH_2Cl_2 (3 mL) was transferred into the flask by syringe. The slurry was stirred for 15 min at −78 °C, cyclobutanone (200 mg, 2.85 mmol) was added, and the reaction mixture was stirred at −78 °C for an additional 15 min. The cooling bath was removed, and a warm (50–60 °C) solution of (*E*,*E*)-1,2-dibenzylidenecyclopentane (773 mg, 3.14 mmol) in benzene (15 mL) was immediately added by syringe. The solution became dark red, and nitrogen evolution occurred. The reaction mixture was stirred at rt for 1 h, maleic anhydride (0.8 g, 8.2 mmol) was added, and the resulting mixture was stirred for 8 h. The dark-red slurry was poured into pentane (150 mL), and insoluble material was removed by vacuum filtration. Concentration of the filtrate followed by chromatography over silica gel using pentane as eluant afforded **10** (R_f=0.45, 12.8 mg, 0.04 mmol, 1.4%) as a colorless solid, and the presumed [2+2] cycloadduct (R_f, 7.8 mg, 0.025 mmol, 0.9%) as an amorphous solid. Analytical GC conditions: initial/temperatures: 120, 250 °C; initial/final time for temperature program: 1, 10 min; ramp rate: 15 °C/min; retention time of **10**: 12.9 min.

Spectral data. ^{1}H NMR: δ 1.72 (2H, m), 1.86 (2H, m), 2.09 (8H, m), 3.86 (2H, s), 7.10–7.33 (10H, s); ^{13}C NMR: δ 22.2, 33.8, 46.1, 126.2, 128.3 (2C), 136.5, 142.5; HRMS *m*/*z* calcd for $C_{24}H_{25}$ 313.1956, found 313.1948.

X-ray crystallographic analysis for **10**: Crystals were grown as colorless blocks by slow evaporation from a two-phase solution of pentane–$CHCl_3$. The data crystal was cut from a larger crystal and had approximate dimensions, 0.35×0.35×0.49 mm^3. The data were collected at −90 °C on a Siemens P3 diffractometer, equipped with a Nicolet LT-2 low-temperature device and using a graphite monochromator with Mo Kα radiation (λ=0.71073 Å).[‖]

5.1.4. Reaction of cyclopentyne with (*E*,*Z*)-1,2-dibenzylidenecyclopentane (5). The procedure used for preparing **10** was used with the following amounts of reagents: KH (542 mg, 4.74 mmol, 35% in mineral oil), DAMP (500 mg, 2.80 mmol), cyclobutanone (166 mg,

[‖] Crystallographic data for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 218855. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax:+44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

2.37 mmol), *E*,*Z*-1,2-dibenzylidenecyclopentane (292 mg, 1.19 mmol), and maleic anhydride (0.3 g, 3 mmol). The filtered pentane solution was concentrated to 10 mL and passed through a short silica plug before analysis by GC to afford 47 mg of crude **14**. GC conditions were the same as used for **10**, and the retention time of **14** was found to be 12.6 min.

5.1.5. 4,8-Diphenyl-1,2,3,5,6,7-hexahydro-*s*-indacene (13). A solution of **10** (23 mg, 0.074 mmol) and DDQ (20 mg, 0.064 mmol) in benzene (5 mL) contained in a 10-mL flask was heated under reflux for 1.5 h, during which time the solution turned from light yellow to dark black. Filtration, concentration, and chromatography over silica gel using ethyl acetate–hexane (1:19) as eluant afforded **13** (R_f (0.49, 15 mg, 0.048 mmol, 75%) as a colorless solid (mp 178–180 °C). Using the same GC conditions as with **10**, the retention time of **13** was 15.9 min.

Spectra data. ^{1}H NMR: δ 1.95 (4H, quintet, J=7 Hz), 2.81 (8H, t, J=7 Hz), 7.26–7.44 (10H, m); ^{13}C NMR: δ 26.2, 32.7, 126.7, 128.8, 129.6, 133.9, 140.3, 141.1; HRMS *m*/*z* calcd for $C_{24}H_{23}$ 311.1799, found 311.1790.

5.1.6. Dehydrogenation of *trans*-4,8-diphenyl-1,2,3,4,5,6,7,8-octahydro-*s*-indacene (14). The procedure used for oxidizing **10** was used with the following amounts of reagents: Crude **14** (47 mg) and DDQ (50 mg, 0.22 mmol). The solution was heated under reflux for 4.5 h, and the color of the solution turned from light yellow to dark black. The resulting solution was vacuum-filtered and concentrated. The crude product was passed through a silica gel plug using ethyl acetate–hexane (1:19) as eluant. Analysis by GC showed that **13** had been formed, and no **14** remained.

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References and notes

1. (a) Gilbert, J. C.; McKinley, E. G.; Hou, D.-R. *Tetrahedron* **1997**, *53*, 9891–9902. (b) Gilbert, J. C.; Hou, D.-R.; Grimme, J. W. *J. Org. Chem.* **1999**, *64*, 1529–1534.
2. (a) Fitjer, L.; Modaressi, S. *Tetrahedron Lett.* **1983**, *24*, 5495–5498. (b) Gilbert, J. C.; Baze, M. E. *J. Am. Chem. Soc.* **1984**, *106*, 1885.
3. (a) Sauer, J.; Sustmann, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 779–807, Reviews:. (b) Li, Y.; Houk, K. N. *J. Am. Chem. Soc.* **1993**, *115*, 7478–7485, and references cited therein.
4. (a) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag-Chemie: Weinheim, 1970. (b) Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; Wiley: New York, 1976.
5. (a) Laird, D. W.; Gilbert, J. C. *J. Am. Chem. Soc.* **2001**, 6706–6707. (b) Bachrach, S. M.; Gilbert, J. C.; Laird, D. W. *J. Am. Chem. Soc.* **2001**, 6708–6709.
6. (a) Wittig, G.; Heyn, J. *Liebigs Ann. Chem.* **1969**, *726*, 57–68. (b) Wittig, G. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 731–737.
7. Olivella, S.; Periciis, M. A.; Riera, A.; Solé, A. *J. Am. Chem. Soc.* **1986**, *108*, 6884–6888.
8. Fitjer, L.; Modaressi, S. *Tetrahedron Lett.* **1982**, *23*, 1661–1664.
9. (a) Sustmann, R.; Böhm, M.; Sauer, J. *Chem. Ber.* **1979**, *112*, 883. (b) Schwager, L.; Vogel, P. *Helv. Chim. Acta* **1980**, *63*, 1176. (c) Castedo, L.; Guitian, E.; Saa, J. M.; Suau, R. *Tetrahedron Lett.* **1982**, *23*, 457. (d) Paquette, L. A.; Schafer, A. G.; Blount, J. F. *J. Am. Chem. Soc.* **1983**, *105*, 3642–3649. (e) Snowden, R. L.; Wüst, M. *Tetrahedron Lett.* **1986**, *27*, 703.
10. (a) Witschard, G.; Griffin, C. E. *J. Org. Chem.* **1964**, *29*, 2335–2340. (b) Overberger, C. G.; Hall, J. R. *J. Org. Chem.* **1961**, *26*, 4359–4364.
11. (a) Baldry, *J. Chem. Soc., Perkin Trans. 1* **1975**, 1913–1920. (b) Yee, W. A.; Hug, S. J.; Kligrt, D. S. *J. Am. Chem. Soc.* **1988**, *110*, 2164–2169. (c) Wakamatsu, K.; Takahashi, Y.; Kikuchi, K.; Miyashi, T. *Tetrahedron Lett.* **1994**, *35*, 5681–5684.
12. (a) Branton, G. R.; Skinner, R. F. *Trans. Faraday Soc.* **1966**, *62*, 1546–1552. (b) Frey, H. M.; Pope, B. M.; Skinner, R. F. *Trans. Faraday Soc.* **1967**, *63*, 1166–1170. (c) Branton, G. R.; Srinivasan, R. *J. Am. Chem. Soc.* **1969**, *91*, 7557–7561. (d) Brauman, J. I.; Archie, W. C. *Tetrahedron* **1971**, *27*, 1275–1280. (e) Miyashi, T.; Wakamatsu, K.; Akiya, T.; Kikuchi, K.; Mukai, T. *J. Am. Chem. Soc.* **1987**, *109*, 5720–5721.
13. Dale, J.; Kristiansen, P. O. *Acta Chem. Scand.* **1972**, *26*, 961–969.
14. (a) Laidler, K. J.; Loucks, L. F. In *Chemical Kinetics*; Bamford, C. H., Tipper, C. F. H., Eds.; Elsevier: New York, 1972; p 35. (b) Cundall, R. B. *Progress in Reaction Kinetics*; Pergamon: Oxford, 1964; Vol. 2, Chapter 4.
15. Bachmann, W. E.; Scott, L. B. *J. Am. Chem. Soc.* **1948**, *70*, 1458–1461.
16. (a) Stoos, F.; Rocek, *J. Am. Chem. Soc.* **1972**, *94*, 2719–2723. (b) Jacobson, B. M.; Soteropoulos, P.; Bahadori, S. *J. Org. Chem.* **1988**, *53*, 3247–3255.
17. Seyferth, D.; Marmor, R. S.; Hilbert, P. H. *J. Org. Chem.* **1971**, *36*, 1379–1386.