# Stereochemistry of Carbenic 1,2-Vinyl Shifts

Wolfgang Kirmse* and Siegfried Kopannia

*Fakultät für Chemie, Ruhr-Universität Bochum, D-44780 Bochum, Germany*

Various 1-phenylbut-3-enylidenes, (Ph)CCR$_2$CH=CHR′, were generated thermally and photolytically from tosylhydrazone (diazo) precursors. 1,2-Vinyl shifts, leading to 1,3-dienes, R′CH=CHC(Ph)=CR$_2$, were found to predominate over γ-C−H insertion (R = Me) and to compete with 1,2-H shifts (R = H). Intramolecular addition to the double bond was detected in the case of R = R′ = Me. The resulting bicyclobutane is thermally stable and does not mediate the vinyl shift. Stereospecific migration of 1-propenyl groups (R′ = Me), with retention of configuration, was observed on thermolysis and direct photolysis of appropriate substrates. These data exclude the intervention of a triplet diradical and point to vinyl migration in the singlet manifold. Benzophenone-sensitized generation of the carbenes led to partial stereomutation but did not provide conclusive evidence for a triplet rearrangement (isomerization of the diene products could not be avoided under these conditions).

When carbenes are generated next to saturated carbon, a 1,2-migration can take place with formation of an alkene.[1] Although the ease of shift can be influenced by nonmigrating ("bystander") substituents, the qualitative ranking of inherent migratory ability appears to be H > Ph > Me. 1,2-H shifts are generally accepted to proceed from the singlet state but can occasionally be "mimicked" by carbene precursors, such as (excited) diazo compounds and diazirines.[2] The multiplicity of aryl migrations is a matter of dispute. The problem is particularly relevant for arylcarbenes, such as **1**, whose spin states equilibrate rapidly. The Ph/H ratios, as reflected by the relative yields of **2** and **3**, tend to increase at low temperatures[3] and to decrease on addition of methanol, a singlet quencher.[4] Both effects suggest that the phenyl group can migrate in the triplet manifold. On the other hand, donor substituents are known to promote aryl shifts.[5] Electron-deficiency of the migrating aryl group points to a dipolar rather than a diradical transition state.
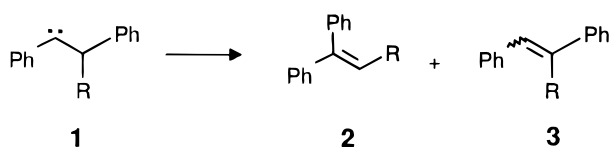
1,2-Vinyl migrations are close analogues of phenyl shifts. Moreover, the stereoisomers (*E/Z*) of 1-alkenyl groups can serve to probe the mechanism. In previous studies, vinyl shifts were induced by decomposition of the diazo compounds **4** (R = Ph, Me).[6,7] Intramolecular C−H insertion (→**6**) and, in the case of R = Ph, addition to π bonds were found to compete with vinyl migration (→**5**). These reactions are not well-suited for mechanistic analysis as the substrates **4** lack geometric isomerism, and spin inversion of the intervening allylcarbenes is presumed to be slow. In the present work, we focus on analogues of **1** in which the migrating phenyl group was replaced with 1-propenyl. We observe that 1,2-shifts of (*E*)- and (*Z*)-1-propenyl groups to the divalent carbon proceed with *retention of configuration*.
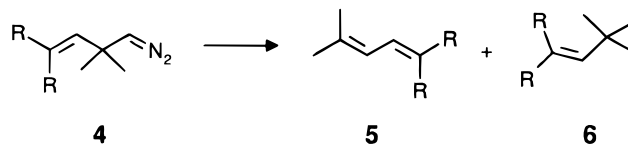


## Results and Discussion

**2,2-Dimethyl-1-phenyl-3-butenylidene (16).** The reactivity of carbenes tends to be lowered by π conjugation. Therefore, we had to make sure that vinyl groups migrate to a phenyl-substituted terminus. As our first model we chose **16**. An indirect route to **16** was pursued by Padwa et al., who studied the flash vacuum pyrolysis (FVP) of the oxadiazolinone **7** at ca. 700 °C.[8] Extrusion of CO$_2$ from **7** is thought to generate the diazo compound **13**, either by a 3,3-sigmatropic shift of the nitrilimine **8** or via **9** (Scheme 1). Decomposition of **13**, with interven-

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**Scheme 1**
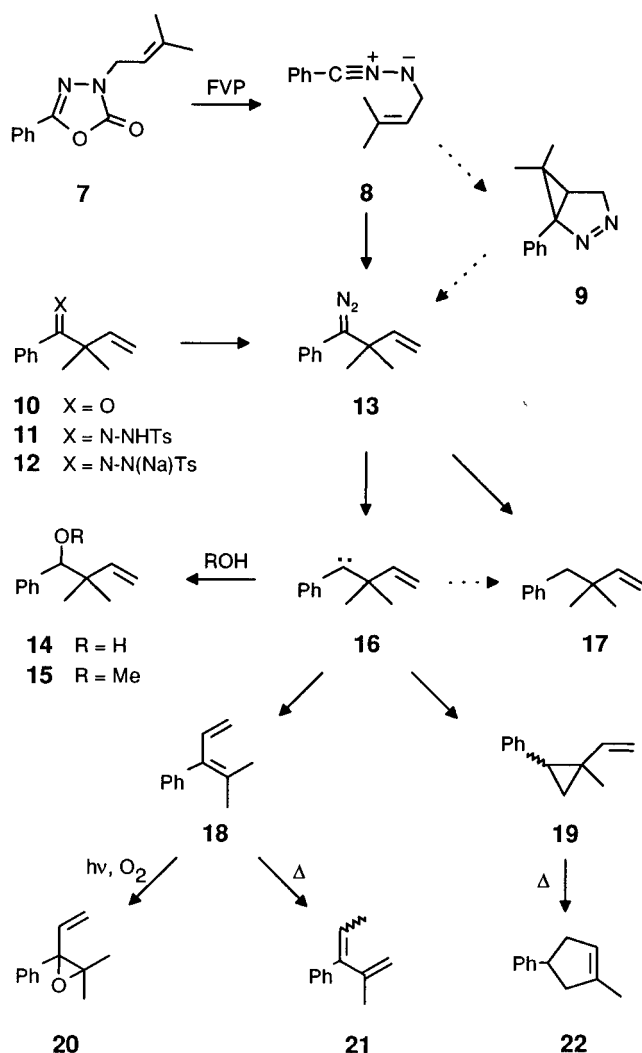


**Table 1. Products from Photolyses[a] of 12**

| conditions | 18 | cis-19 | trans-19 | 14 | 15 | 17 | yield (%) |
|---|---|---|---|---|---|---|---|
| diglyme | 43.6 | 34.6 | 21.8 | | | | 70 |
| diglyme, Ph₂CO[b] | 10.2 | 28.2 | 18.1 | | | 43.5 | 18 |
| water | 38.9 | 29.0 | 26.2 | 5.9 | | | 30 |
| MeOH | 41.2 | 22.4 | 20.4 | | 16.0 | | 50 |
| MeOH, Ph₂CO[b] | 42.6 | 25.6 | 17.1 | | 14.7 | trace | 16 |

[a] Pyrex vessel, medium presure mercury arc, 0.046 M **12**, 20 °C, 30 min. [b] 1.6 equiv, 0.073 M.

tion of the carbene **16**, should lead to **18** (by 1,2-vinyl shift) and **19** (by C–H insertion). The products actually obtained on pyrolysis of **7** were **21** (45%) and **22** (25%). Most likely, **21** arises from **18** by 1,5-H shift, and vinylcyclopropane rearrangement of **19** affords **22**.

Although the formation of **21** indicates that the vinyl shift **16 → 18** does occur at high temperatures, less vigorous conditions and a more straightforward approach were desirable. Base-induced cleavage of the tosylhydrazone **11** provided pentane solutions of the diazo compound **13**, $\nu(N_2) = 2055 \text{ cm}^{-1}$. When these solutions were photolyzed, only 0.5% of **18** and **19** was formed. Much better yields were obtained on photolysis of the tosylhydrazone sodium salt **12** in diglyme (1,1′-oxybis[2-methoxyethane]) (Table 1). On prolonged irradiation, **18** was converted into the oxirane **20**. The apparent oxidation was accelerated by the presence of oxygen but also

occurred in degassed solutions. Intramolecular reactions of **16** prevail even in protic solvents; only a fraction of the carbene is intercepted by O–H insertion. Somewhat unexpectedly, the yield of **14** (in water) was inferior to that of **15** (in methanol). Aqueous solutions of **12** became turbid on photolysis as **13**, and products derived therefrom were formed as a dispersed organic phase. The heterogeneity of the aqueous medium impedes O–H insertion, as compared with the homogeneous solution in methanol.

In diglyme, benzophenone sensitization gave rise to **17** at the expense of **18**. The triplet-induced transformation, $R_2CN_2 \rightarrow R_2CH_2$, does not necessarily involve a carbene intermediate, as was discussed elsewhere.[9] Moreover, **18** was converted into nonvolatile products (polymers?) when irradiated in the presence of benzophenone. In view of these side reactions, a comparison of direct and sensitized photolyses of **12** in diglyme is not meaningful. In contrast, the product distribution obtained from methanolic solutions of **12** was but slightly affected by triplet sensitization (Table 1). These data point to a spin-equilibrated intermediate.

Conspicuously absent from the photolysis mixtures is the product of intramolecular addition, **23**. Since thermal rearrangements of bicyclobutanes are known to give 1,3-dienes,[10] the question arises whether **18** could be formed by way of **23**. This route is inconsistent with the properties of **23** which was reportedly distilled at 55 °C/3 Torr.[11] Moreover, pyrolysis of the closely related 1,2,2-trimethylbicyclo[1.1.0]butane (**24**) at 300 °C gave nearly equimolar amounts of **25** (53%) and **26** (47%).[12] The phenyl analogue of **26**, 4-methyl-2-phenyl-1,3-pentadiene, was not obtained from photolyses of **2**. Therefore, a direct 1,2-vinyl shift, **16 → 18**, appears most likely.
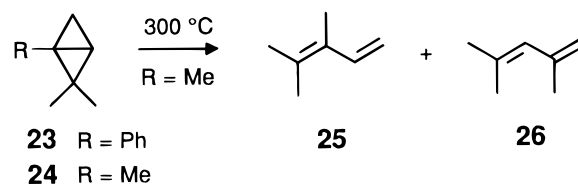


**2,2-Dimethyl-1-phenyl-3-pentenylidene (33).** Repeated alkylation of 1-phenyl-(*E*)-3-penten-1-one (*E*-**27**) with MeI–LDA provided *E*-**28**[13] (Scheme 2). The analogous methylation of *Z*-**27** could not be carried to completion, but *Z*-**28** was isolated from the resulting mixture by HPLC. While *E*-**28** was smoothly converted into the tosylhydrazone *E*-**29**, the forcing conditions required for *Z*-**28** led to partial *Z* → *E* isomerization (NMR). Attempts to separate the product mixture failed. Therefore, our studies were limited to the generation and reactions of *E*-**33**.

Flash vacuum pyrolysis of the tosylhydrazone sodium salt *E*-**30** at ca. 280 °C gave equimolar amounts of the bicyclobutane **35** (by intramolecular addition) and the diene *E*-**36** (by 1,2-vinyl shift). Photolyses of *E*-**30** in diglyme produced some cyclopropane **37** (by C–H insertion) in addition to **35** and **36** (Table 2). When *E*-**30** was

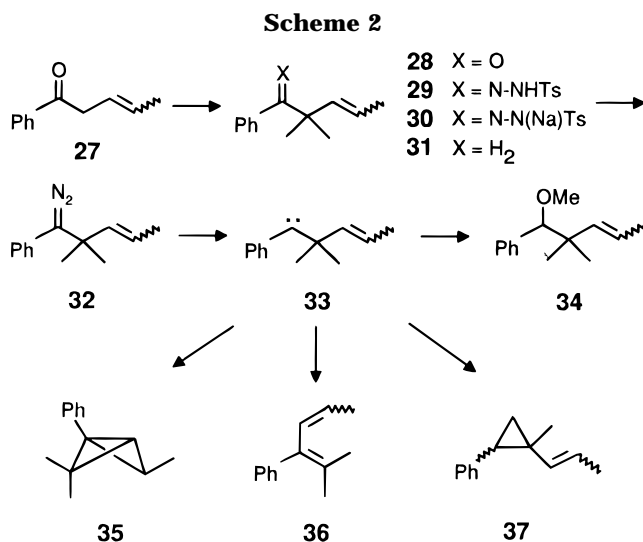(9) Guth, M.; Kirmse, W. *Acta Chem. Scand.* **1992**, *46*, 606.
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**Scheme 2**

28  X = O
29  X = N-NHTs
30  X = N-N(Na)Ts
31  X = H₂

32          33          34

35          36          37

photolyzed in methanol, the ether **34** was also present in the product mixture. Sensitization with benzophenone seemingly enhances the yield of **34** at the expense of **35**. However, these changes are largely due to the fact that the products decay at different rates, **35** > **36** > **34**, on benzophenone-sensitized irradiation (see Experimental Section). Therefore, the quantitative results of sensitized photolyses should be interpreted with caution. Although *E*-**36** prevailed in all reactions, minor amounts of *Z*-**36** were also found, particularly in the presence of benzophenone. The stereochemical "leakage" may be associated with the 1,2-vinyl shift, but light-induced *E/Z* isomerization of substrate and/or product is also possible. This point was not clarified, as the lack of pure *Z* substrate precluded a complete stereochemical analysis. A more significant result is the persistence of the bicyclobutane **35**. The thermal stability of **35** suggests that bicyclobutanes should have been detected if formed from the carbenes **16** (above) and **42** (below).

**1-Phenyl-3-pentenylidene (42).** 1,2-Hydrogen shifts of carbenes[1] and, in some cases, of carbene precursors[2] proceed rapidly, often to the exclusion of competing reactions. Therefore, our first choice for the present work was **33** rather than **42**. However, in view of our failure to generate *Z*-**33**, we resorted to the parent system. Fortunately, **42** was found to undergo the 1,2-vinyl shift (→**44**), albeit to a lesser extent than **33** (Scheme 3).

The tosylhydrazones *E*-**38** and *Z*-**38** were described by Padwa et al., who studied the intramolecular cycloaddition of the diazo compound **40** but did not explore the carbenic reactivity.[14] Flash vacuum pyrolysis of the sodium salt *E*-**39** afforded *E*-**44** as well as *E*-**45** and *E*-**46** (Table 3). The double bond newly formed by 1,2-H shift assumes both the *E* and *Z* geometry while the configuration at C-4 is retained in all products. This does not hold for photolyses of *E*-**39**, which gave rise to *Z*-**45** and *Z*-**46** in addition to *E*-**44**, *E*-**45**, *E*-**46**, and, in methanol, *E*-**43**. The *Z*-dienes were not detected at low conversions; hence they are likely to arise by photoisomerization of *E*-**45** and *E*-**46**, respectively.

The thermolysis of *Z*-**39** proceeded stereospecifically, with exclusive formation of *Z*-**44**, *Z*-**45**, and *Z*-**46**. The formation of *E* isomers on direct photolysis of *Z*-**39** was

minimized by low conversion and eliminated by irradiation with light of ≥400 nm, using a NaNO₂ filter (Table 4). Substantial *Z* → *E* isomerization of the 1,3-dienes occurred in benzophenone-sensitized photolyses, whereas **41** and **43** were exclusively *Z*. These observations point to the configurational integrity of the substrate. Controls confirmed that the 1,3-dienes **44**, **45**, and **46** undergo geometrical isomerization on direct (<400 nm) as well as sensitized irradiation. Nevertheless, nonstereospecific rearrangements of triplet **42** cannot be definitively excluded.

## Summary and Conclusion

1,2-Vinyl shifts of 1-phenylbut-3-enylidenes (**47**), leading to 1,3-dienes (**48**), prevail over γ-C−H insertion (R = Me) and compete with 1,2-H shifts (R = H). Intramolecular addition to the double bond occurs only in the case of R = R′ = Me. The resulting bicyclobutane is thermally stable and does not mediate the vinyl shift. Stereospecific migration of 1-propenyl groups (R′ = Me), with retention of configuration, excludes an intermediate **49**, which is capable of rotation about the exocyclic C−C bond. Such rotation would be anticipated if **49** were a triplet diradical. Our data demonstrate that 1,2-vinyl shifts do proceed in the singlet manifold. Therefore, analogous phenyl shifts should not be dismissed a priori.

47          48

49
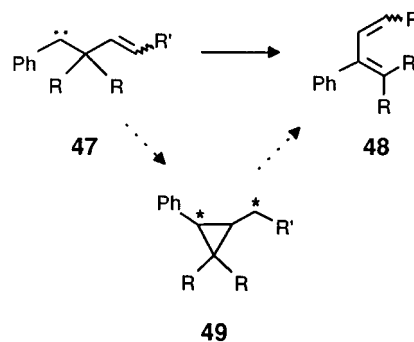
## Experimental Section

**General.** Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. ¹H NMR spectra were recorded at 80 and/or 400 MHz. Chemical shifts (δ) are reported as units (ppm) downfield from tetramethylsilane as an internal standard. Gas chromatography (GC) was performed on glass capillary columns of 0.25−0.38 mm diameter (length, stationary phase, and temperature for the individual mixtures are given below). Packed glass columns were used for preparative gas chromatography (PGC). High-pressure liquid chromatography (HPLC) was performed on stainless steel columns 300 × 5 mm i.d. (analytical) and 300 × 25 mm i.d. (preparative), employing refractometric detection. The apparatus used for the flash vacuum pyrolysis of tosylhydrazone sodium salts (280−300 °C, 10⁻³ Torr) has been described elsewhere.[15] Photolyses were carried out using a 150-W medium-pressure mercury arc lamp in a water-cooled Pyrex immersion well (ca. 10 mm i.d.). In some experiments, 0.1 M NaNO₂ was circulated through the immersion well (λ ≥ 400 nm).[16] Pyrex cylindrical vessels or tubes containing the samples were strapped around this well, and the assembly was immersed in a water bath held at 20 °C.

**Preparation of Tosylhydrazone Sodium Salts.** To a solution of the tosylhydrazone (1 mmol) in 5 mL of anhydrous

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**Table 2. Products Obtained from 30**

| conditions | E-31 | E-34 | 35 | E-36 | Z-36 | 37 cis-E | cis-Z | trans-E | yield (%) |
|---|---|---|---|---|---|---|---|---|---|
| FVP,[a] 280 °C | | | 50.7 | 49.3 | | | | | 66 |
| hv[b], diglyme | | | 41.1 | 47.5 | | 4.6 | | 6.8 | 74 |
| hv[c], diglyme, 0.2 M Ph$_2$CO | 5.3 | | 39.6 | 44.7 | 4.4 | | | 6.0 | 16 |
| hv[b], MeOH, 0.2 M NaOMe | | 11.8 | 37.5 | 41.6 | 2.0 | 1.6 | 3.7 | 1.8 | 64 |
| hv[c], MeOH, 0.2 M NaOMe, 0.4 M Ph$_2$CO | 6.8 | 33.6 | 5.9 | 43.1 | 6.3 | 1.5 | 2.2 | 0.6 | 15 |

[a] Flash vacuum pyrolysis ($10^{-3}$ Torr). [b] 60 min. [c] 30 min.

**Scheme 3**



38  X = N-NHTs
39  X = N-N(Na)Ts
40  X = N$_2$
41  X = H$_2$
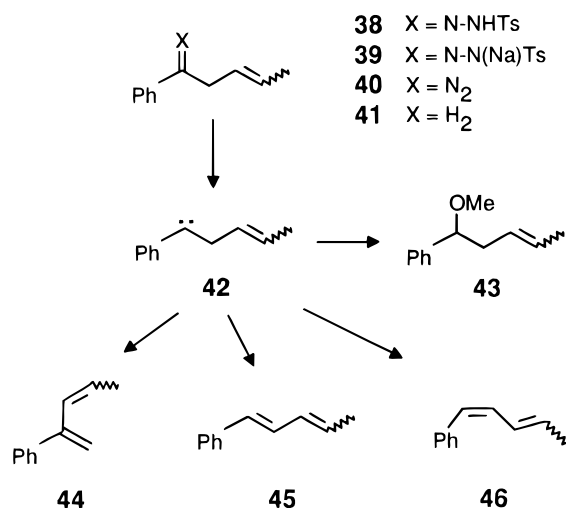
**Table 3. Products Obtained from E-39**

| conditions | E-41 | E-43 | E-44 | E-45 | Z-45 | E-46 | Z-46 | yield (%) |
|---|---|---|---|---|---|---|---|---|
| FVP,[a] 280 °C | | | 32.1 | 52.4 | | 15.5 | | 72 |
| hv, diglyme | | | 10.1 | 45.1 | 6.1 | 27.1 | 11.6 | 68 |
| hv, diglyme, t → 0 | | | 8.0 | 57.9 | | 34.1 | | |
| hv, diglyme, 0.4 M Ph$_2$CO | 10.1 | | 7.2 | 47.5 | 12.3 | 16.7 | 6.2 | 17 |
| hv, MeOH[b] | | 11.3 | 13.1 | 50.0 | 3.0 | 21.4 | 1.2 | 49 |
| hv, MeOH,[b] 0.2 M Ph$_2$CO | 4.6 | 26.5 | 14.8 | 31.0 | 9.4 | 9.9 | 3.8 | 25 |
| hv, MeOH,[b] 0.4 M Ph$_2$CO | 4.3 | 30.9 | 15.3 | 24.9 | 9.1 | 10.5 | 5.0 | 17 |

[a] Flash vacuum pyrolysis ($10^{-3}$ Torr). [b] 0.2 M NaOMe.

THF was added 1 mmol of sodium hydride (as a suspension in mineral oil). The mixture was stirred for 30 min at room temperature, *n*-pentane (40−50 mL) was added, and stirring was continued for 30 min. The precipitated sodium salt was filtered with suction, washed with *n*-pentane, and dried in vacuo. If the sodium salt failed to crystallize, the solvent was removed in vacuo, and the residue was triturated with pentane in an ultrasound bath. Moisture and light should be excluded during these processes.

**2,2-Dimethyl-1-phenylbut-3-en-1-one Tosylhydrazone (11).** To a solution of *p*-toluenesulfonylhydrazine (11.4 g, 60 mmol) in methanol (50 mL) was added 2,2-dimethyl-1-phenylbut-3-en-1-one (10)[17] (10.2 g, 60 mmol). After the mixture was heated at reflux for 1 h, it was allowed to stand at room temperature for 48 h. The precipitate was filtered off and recrystallized from ethanol to give 12.9 g (63%) of 11: mp 105 °C; ^{1}H NMR (CDCl$_3$) $\delta$ 1.2 (s, 6 H), 2.45 (s, 3 H), 4.9 (ddd, $J =$ 17, 11, 1 Hz, 2 H), 5.75 (dd, $J =$ 17, 11 Hz, 1 H), 6.7−7.0 (m, 4 H), 7.2−7.4 (m, 3 H), 7.7−7.9 (m, 2 H). Anal. Calcd for C$_{19}$H$_{22}$N$_2$O$_2$S: C, 66.67; H, 6.43; N, 8.19. Found: C, 66.59; H, 6.49; N, 8.22.

**Reaction Products of 2,2-Dimethyl-1-phenyl-3-butenylidene (16).** Solutions of the diazo compound 13 were

prepared according to a published procedure.[18] The products obtained from thermolyzes and photolyzes of 12 or 13 (for reaction conditions, see Table 1) were analyzed by GC (18 m OV17, 140 °C, and 30 m Marlophen, 110 °C) and separated by HPLC (Si 60-5-C18, methanol−water = 75:25). Yields were estimated by GC, using dodecane as an internal standard (Table 1). When 12 was photolyzed in diglyme, the epoxide 20 appeared after 60 min and increased to ca. 8% after 120 min. Saturation with oxygen promoted the formation of 20 (7% after 50 min, 10% after 90 min). Under these conditions, 20 was also formed by irradiation of 18.

The structures attributed to the reaction products were corroborated by synthesis. Wolff−Kishner reduction of 10 (1,2-ethanediol, 150 °C, 3 h) gave 3-methyl-4-phenyl-1-butene (17)[19] (64%), ^{1}H NMR (CDCl$_3$) $\delta$ 1.0 (s, 6 H), 2.55 (s, 2 H), 4.9 (ddd, $J =$ 17, 10, 1.5 Hz, 2 H), 5.9 (dd, $J =$ 17, 10 Hz, 1 H), 7.0−7.3 (m, 5 H). Dehydration of 4-methyl-3-phenyl-1-penten-3-ol[20] (8.0 g, 45 mmol) with 0.8 g of 85% phosphoric acid (80 °C, 3 h) afforded 4-methyl-3-phenyl-1,3-pentadiene[21] (18, 15%) along with 2-methyl-3-phenyl-1,3-pentadiene[8] (21, 12%) and 3-iso-propylindene[22] (61%). The alkenes were separated by HPLC (Si 60-5-C18, methanol−water = 75:25). Oxidation of 18 (peracetic acid−sodium acetate in CH$_2$Cl$_2$, 20 °C, 16 h) gave 65% of 2,2-dimethyl-3-ethenyl-3-phenyloxirane (20): ^{1}H NMR (CDCl$_3$) $\delta$ 1.0 (s, 3 H), 1.4 (s, 3 H), 5.2 (ddd, $J =$ 17, 11, 2 Hz, 2 H), 6.15 (dd, $J =$ 17, 11 Hz, 1 H), 7.2−7.4 (m, 5 H); ^{13}C NMR (CDCl$_3$) $\delta$ 20.1 (CH$_3$), 21.9 (CH$_3$), 65.5 (C), 69.7 (C), 118.3 (CH$_2$), 126.9 (CH), 127.1 (CH), 128.0 (CH), 136.5 (CH), 138.8 (C). 1-Ethenyl-1-methyl-2-phenylcyclopropane (19, *E*,*Z* mixture) was obtained by benzylidene transfer to isoprene.[23] Since separation of the isomers on a preparative scale failed, *trans*-(1-methyl-2-phenylcyclopropyl)methanol (*trans*-50)[24] was oxidized (MnO$_2$, benzene, 45 h reflux) to the analogous aldehyde 51 which was converted into *trans*-19 by methylenation (Ph$_3$PCH$_3$Br, NaH, DMSO, 90 °C, 2 h). The cis/trans assignment of 19 by NMR[23] was thus confirmed.



50  X = CH$_2$OH
51  X = CHO
19  X = CH=CH$_2$
X = CO$_2$Et
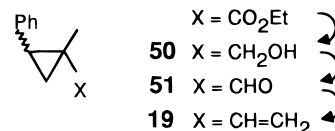
**2,2-Dimethyl-1-phenylbut-3-en-1-ol (14) and 3,3-Dimethyl-4-methoxy-4-phenylbutene (15).** To a solution of 10 (0.80 g, 4.6 mmol) in ether (10 mL) was added a solution of NaBH$_4$ (0.35 g, 9.2 mmol) in 0.1 N NaOH (5 mL). After the biphasic mixture was stirred vigorously for 16 h, the phases were separated. The ether solution was washed with water, dried (MgSO$_4$), and concentrated in vacuo to give 0.62 g (76%) of crude (GC: 91%) 14, which was purified by PGC (0.5 m OV101, 100 °C): ^{1}H NMR (CDCl$_3$) $\delta$ 0.95 (s, 3 H), 1.0 (s, 3 H), 4.45 (d, $J =$ 3 Hz, 1 H), 5.05 (ddd, $J =$ 17, 11, 1.5 Hz, 2 H), 5.9 (dd, $J$

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**Table 4. Products Obtained from Z-39**

| conditions | Z-41 | Z-43 | E-44 | Z-44 | E-45 | Z-45 | E-46 | Z-46 | yield (%) |
|---|---|---|---|---|---|---|---|---|---|
| FVP,[a] 280 °C | | | | 34.5 | | 43.1 | | 22.4 | 69 |
| *hv*, diglyme | | | 5.7 | 10.1 | 21.1 | 28.5 | 16.4 | 18.2 | 69 |
| *hv*, diglyme, *t* → 0 | | | trace | 7.9 | trace | 66.4 | 2.2 | 23.5 | |
| *hv*, diglyme, ≥400 nm[b] | | | | 8.9 | | 73.1 | | 18.0 | |
| *hv*, diglyme, 0.4 M Ph₂CO | 18.3 | | 1.5 | 4.7 | 15.6 | 33.1 | 8.2 | 18.6 | 17 |
| *hv*, MeOH[c] | | 11.3 | | 12.2 | 5.3 | 52.8 | 1.3 | 17.1 | 80 |
| *hv*, MeOH,[c] 0.2 M Ph₂CO | 1.1 | 23.7 | 6.5 | 8.7 | 8.3 | 41.8 | 1.6 | 8.3 | 37 |
| *hv*, MeOH,[c] 0.4 M Ph₂CO | 1.7 | 21.1 | 6.9 | 7.3 | 10.5 | 39.2 | 3.0 | 10.3 | 23 |

[a] Flash vacuum pyrolysis ($10^{-3}$ Torr). [b] Filtered with 0.1 M $NaNO_2$. [c] 0.2 M NaOMe.

= 17, 11 Hz, 1 H), 7.2–7.3 (m, 5 H). Anal. Calcd for $C_{12}H_{16}O$: C, 81.82; H, 9.09. Found: C, 81.91; H, 9.16. The alcohol **10** was previously obtained from a Wittig rearrangement but no analytical data were reported.[25]

To a suspension of pentane-washed NaH (40 mg, 1.6 mmol) in anhydrous THF (10 mL) was added **14** (0.18 g, 1 mmol). The mixture was heated at reflux for 30 min. Methyl iodide (0.30 g, 2.1 mmol) was then added, and heating at reflux was continued for 30 min. The mixture was partitioned between water and ether. The combined ether solutions were dried ($MgSO_4$) and concentrated in vacuo to give 0.17 g (73%) of **15** which was purified by PGC (0.5 m OV101, 100 °C): $^1H$ NMR ($CDCl_3$) δ 0.95 (s, 3 H), 1.0 (s, 3 H), 3.15 (s, 3 H), 4.9 (ddd, *J* = 17, 11, 1.5 Hz, 2 H), 5.9 (dd, *J* = 17, 11 Hz, 1 H), 7.1–7.35 (m, 5 H). Anal. Calcd for $C_{13}H_{18}O$: C, 82.11; H, 9.47. Found: C, 82.02; H, 9.55.

**3-Methyl-4-phenyl-1,3-pentadiene (54).** The diene **54** was of interest as the product resulting from a 1,2-methyl shift of the carbene **16**. Freshly prepared $MnO_2·H_2O$ (3.9 g, 40 mmol) was dehydrated by azeotropic distillation with benzene (70 mL). 2-Methyl-3-phenyl-2-buten-1-ol (**52**)[26] (*E,Z* mixture, 1.6 g, 10 mmol) was then added. Azeotropic distillation of the nitrogen-blanketed mixture was continued for 45 h while progress of the reaction was monitored by GC. After being cooled to room temperature, the benzene solution was filtered, dried ($MgSO_4$), and concentrated to give 1.5 g (95%) of crude 2-methyl-3-phenyl-2-butenal (**53**, *E*:*Z* = 3:1): IR ($CDCl_3$) 1670 cm⁻¹ (C=O); $^1H$ NMR ($CDCl_3$) δ 1.65 (q, *J* = 1 Hz, 0.75 H), 1.9 (q, *J* = 1 Hz, 2.25 H), 2.25 (q, *J* = 1 Hz, 2.25 H), 2.45 (q, *J* = 1 Hz, 0.75 H), 7.0–7.5 (m, 5 H), 9.45 (s, 0.75 H), 10.3 (s, 0.25 H).
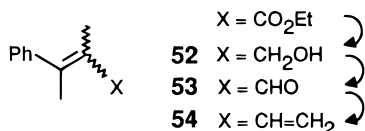


To anhydrous DMSO (10 mL) was added sodium hydride (60% in mineral oil, 0.4 g, 10 mmol). The mixture was heated under nitrogen at 80 °C for 45 min and then cooled to 0 °C. A solution of methyltriphenylphosphonium bromide (3.6 g, 10 mmol) in DMSO (20 mL) was added. After the mixture was stirred at 0 °C for 10 min, **53** (1.5 g, 9.5 mmol) was added. The solution was heated at 90 °C for 2 h and was then partitioned between water and pentane. The combined pentane extracts were washed with water, dried ($MgSO_4$), and concentrated in vacuo to give 1.4 g (93%) of **54**, *E*:*Z* = 71:29 (GC), which was purified by PGC (1.5 m OV101, 100 °C): $^1H$ NMR ($CDCl_3$) δ 1.75 (q, *J* = 1.5 Hz, 0.9 H), 2.0 (q, *J* = 1.5 Hz, 2.1 H), 2.15 (q, *J* = 1.5 Hz, 2.1 H), 2.2 (q, *J* = 1.5 Hz, 0.9 H), 5.1 (ddd, *J* = 17, 11, 1 Hz, 2 H), 6.55 (dd, *J* = 17, 11 Hz, 1 H), 7.0–7.5 (m, 5 H). Anal. Calcd for $C_{12}H_{14}$: C, 91.14; H, 8.86. Found: C, 91.00; H, 8.94. By means of this sample, the presence of **54** among the reaction products of **16** was definitively excluded.

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(26) Shono, T.; Nishiguchi, I.; Komamura, T.; Fujita, K. *Tetrahedron Lett.* **1977**, 4327.

**2,2-Dimethyl-1-phenyl-3-penten-1-one Tosylhydrazone (29).** Following a method similar to the preparation of **11**, 2,2-dimethyl-1-phenyl-(*E*)-4-penten-1-one (**28**)[13] (2.5 g, 13.3 mmol) and *p*-toluenesulfonylhydrazine (2.5 g, 13.5 mmol) afforded 3.1 g (65%) of (*E*)-**29**: mp 104 °C; $^1H$ NMR ($CDCl_3$) δ 1.1 (s, 6 H), 1.5 (dd, *J* = 6, 1 Hz, 3 H), 2.4 (s, 3 H), 5.15 (dq, *J* = 16, 6 Hz, 1 H), 5.25 (dq, *J* = 16, 1 Hz, 1 H), 6.7–7.8 (m, 9 H). Anal. Calcd for $C_{20}H_{24}N_2O_2S$: C, 67.39; H, 6.79; N, 7.86. Found: C, 67.38; H, 6.77; N, 7.92.

A flask was charged with diisopropylamine (3.55 g, 35 mmol), HMPT (6.25 g, 35 mmol), and THF (25 mL) under nitrogen. To the stirred solution was added at 0 °C *n*-butyllithium (1.6 M in hexane, 21.9 mL, 35 mmol). The mixture was stirred at 0 °C for 30 min and was then cooled to −65 °C. A solution of 1-phenyl-(*Z*)-3-penten-1-one (*Z*-**27**)[14] (3.0 g, 18.8 mmol) in THF (5 mL) was added, and stirring was continued at −65 °C for 30 min. After the mixture was allowed to warm slowly to 0 °C, a solution of methyl iodide (11.4 g, 80 mmol) in THF (10 mL) was added. The reaction mixture was stirred for an additional 2 h at 0 °C and was then partititoned between ether and water. The combined ether solutions were washed with water, dried ($MgSO_4$), and concentrated to give 2.7 g of a product mixture (1:1 by GC). Separation by HPLC (Si 60-5-C18, methanol–water = 4:1) afforded 1.1 g (34%) of 2-methyl-1-phenyl-(*Z*)-3-penten-1-one [IR ($CDCl_3$) 1690 cm⁻¹ (C=O); $^1H$ NMR ($CDCl_3$) δ 1.25 (d, *J* = 7 Hz, 3 H), 1.75 (dd, *J* = 6.5, 1.5 Hz, 3 H), 4.4 (dq, *J* = 9, 7 Hz, 1 H), 5.5 (ddq, *J* = 11, 9, 1.5 Hz, 1 H), 5.55 (dqd, *J* = 11, 6.5, 0.5 Hz, 1 H), 7.4–7.6 (m, 3 H), 7.9–8.0 (m, 2 H)] and 1.2 g (35%) of 2,2-dimethyl-1-phenyl-(*Z*)-3-penten-1-one (*Z*-**28**) [IR ($CDCl_3$) 1680 cm⁻¹ (C=O); $^1H$ NMR ($CDCl_3$) δ 1.35 (dd, *J* = 7, 1.5 Hz, 3 H), 1.4 (s, 6 H), 5.45 (dq, *J* = 11, 7 Hz, 1 H), 5.8 (dq, *J* = 11, 1.5 Hz, 1 H), 7.3–7.5 (m, 3 H), 8.0–8.1 (m, 2 H)].

To a solution of *p*-toluenesulfonylhydrazine (0.8 g, 4.4 mmol) in 0.05 M HCl–MeOH (10 mL) was added *Z*-**28** (0.8 g, 43 mmol). After heating at reflux for 2 h, the dark mixture was partitioned between ether and water. The combined ether solutions were dried ($MgSO_4$) and concentrated in vacuo. HPLC (Si 60-5-C18, methanol–water = 4:1) gave 0.6 g of unreacted ketone and 15 mg (1%) of a mixture (ca. 1:1) of *E*- and *Z*-**29**: $^1H$ NMR ($CDCl_3$) δ 1.1 (s, 3 H), 1.2 (s, 3 H), 1.25 (dd, *J* = 7, 1.5 Hz, 1.5 H), 1.5 (dd, *J* = 6, 1 Hz, 1.5 H), 2.38 (s, 1.5 H), 2.4 (s, 1.5 H), 5.1 (dq, *J* = 11, 1.5 Hz, 0.5 H), 5.15 (dq, *J* = 16, 6 Hz, 0.5 H), 5.25 (dq, *J* = 16, 1 Hz, 0.5 H), 5.35 (dq, *J* = 11, 7 Hz, 0.5 H), 6.7–7.8 (m, 9 H). Attempts to separate the mixture failed, as did attempts to react *Z*-**28** under less forcing conditions.

**Reaction Products of 2,2-Dimethyl-1-phenyl-(*E*)-3-pentenylidene (33).** The reaction products obtained from thermolyses and photolyses of **29** were analyzed by GC (37 m OV17, 140 °C, and 28.5 m Marlophen, 140 °C). Yields were estimated with dodecane as an internal standard (Table 2). Prolonged direct irradiation (up to 2 h) had no significant effect on product distributions. Triplet sensitization, however, led to substantial changes which were mimicked by controls. Thus the bicyclobutane **35** decayed rapidly (15 min, 56.5%; 30 min, 75.8%; 60 min, 93.3%), without formation of volatile products, when irradiated in MeOH, 0.2 M NaOMe, 0.4 M Ph₂CO. Under similar conditions, 30% of the diene **36** was lost after 30 min and a *E*:*Z* ratio of ca. 3 was established. No significant decay (30 min, <5%) and *E/Z* isomerization of the ether **34**

were observed. The products were identified by comparison with samples from appropriate syntheses. The preparation of 1-phenyl-2,2,*exo*-4-trimethylbicyclo[1.1.0]butane (**35**) [$^1$H NMR (CDCl$_3$) $\delta$ 0.88 (d, $J = 6$ Hz, 3 H), 0.90 (s, 3 H), 0.95 (s, 3 H), 1.6 (br s, 1 H), 1.9 (br q, $J = 6$ Hz, 1 H), 7.15–7.25 (m, 5 H)] has been reported.[26] For the remaining products, see below.

**4,4-Dimethyl-5-phenyl-2-pentene (31).** Following a method similar to the preparation of **54**, the ylide derived from ethyltriphenylphosphonium iodide (2.5 g, 6.2 mmol) and NaH (60%, 0.25 g, 62 mmol) in DMSO (5 mL) reacted with 2,2-dimethyl-3-phenylpropanal[27] (0.5 g, 3.1 mmol) to give 0.4 g (80%) of crude **31**, $E{:}Z = 3{:}7$. The mixture was separated by PGC (3 m Apiezon, 150 °C). *E*-**31**: $^1$H NMR (CDCl$_3$) $\delta$ 0.95 (s, 6 H), 1.65 (dd, $J = 6.5$, 1.5 Hz, 3 H), 2.55 (s, 2 H), 5.2 (dq, $J = 16$, 6.5 Hz, 1 H), 5.45 (dq, $J = 16$, 1.5 Hz, 1 H), 7.05–7.25 (m, 5 H). *Z*-**31**: $^1$H NMR (CDCl$_3$) $\delta$ 1.1 (s, 6 H), 1.62 (dd, $J = 7$, 1.5 Hz, 3 H), 2.65 (s, 2 H), 5.2 (dq, $J = 12$, 7 Hz, 1 H), 5.45 (dq, $J = 12$, 1.5 Hz, 1 H), 7.1–7.25 (m, 5 H). Anal. Calcd for C$_{13}$H$_{18}$: C, 89.59; H, 10.41. Found: C, 89.48; H, 10.33.

**4,4-Dimethyl-5-methoxy-5-phenyl-(E)-2-pentene (E-34).** To a stirred, refluxing solution of *E*-**28** (0.6 g, 3.2 mmol) in methanol (5 mL) was added NaBH$_4$ (0.25 g, 6.6 mmol). After cooling to room temperature over 4 h, the mixture was partitioned between water and pentane. The combined pentane solutions were dried (MgSO$_4$) and concentrated in vacuo. GC indicated a 1:1 mixture of ketone and alcohol which was separated by HPLC (Si-60-5, ether–hexane = 1:1). 2,2-Dimethyl-1-phenyl-(*E*)-3-penten-1-ol: $^1$H NMR (CDCl$_3$) $\delta$ 0.9 (s, 3 H), 0.95 (s, 3 H), 1.7 (br d, $J = 7$ Hz, 3 H), 4.4 (m, 1 H), 5.3–5.6 (m, 2 H), 7.3 (br s, 5 H). Anal. Calcd for C$_{13}$H$_{18}$O: C, 82.06; H, 9.53. Found: C, 82.05; H, 9.52.

Following the procedure described for **15**, 2,2-dimethyl-1-phenyl-(*E*)-3-penten-1-ol (0.19 g, 1.0 mmol) was treated with NaH (50 mg, 2.1 mmol) and methyl iodide (0.6 g, 4 mmol) to give 0.19 g (93%) of **34**: $^1$H NMR (CDCl$_3$) $\delta$ 0.9 (s, 3 H), 0.95 (s, 3 H), 1.65 (d, $J = 6$ Hz, 3 H), 3.15 (s, 3 H), 3.8 (s, 1 H), 5.0–5.7 (m, 2 H), 7.1–7.35 (m, 5 H). Anal. Calcd for C$_{14}$H$_{20}$O: C, 82.30; H, 9.87. Found: C, 82.38; H, 9.80.

**2-Methyl-3-phenyl-2,4-hexadiene (36).** To a solution of 1-propenylmagnesium bromide, prepared from magnesium (3.7 g, 0.12 mol) and 1-bromopropene (18.1 g, 0.15 mol) in THF (160 mL), was added a solution of isobutyrophenone (18.0 g, 0.12 mol) in THF (30 mL). The mixture was heated at reflux for 2 h. Conventional workup afforded 18.0 g (79%) of 2-methyl-3-phenyl-4-hexen-3-ol (**55**) whose *E,Z* isomers (1:3, GC) were separated by chromatography (silica gel, hexane–ether = 4:1). *Z*-**55**: $^1$H NMR (CDCl$_3$) $\delta$ 0.8 (d, $J = 7$ Hz, 3 H), 0.95 (d, $J = 7$ Hz, 3 H), 1.6 (dd, $J = 7$, 1 Hz, 3 H), 2.1 (sept, $J = 7$ Hz, 1 H), 5.65 (dq, $J = 11$, 7 Hz, 1 H), 6.0 (dq, $J = 11$, 1 Hz, 1 H), 7.1–7.55 (m, 5 H). *E*-**55**: $^1$H NMR (CDCl$_3$) $\delta$ 0.75 (d, $J = 7$ Hz, 3 H), 0.9 (d, $J = 7$ Hz, 3 H), 1.75 (dd, $J = 7$, 1 Hz, 3 H), 2.15 (sept, $J = 7$ Hz, 1 H), 5.3–6.1 (m, 2 H), 7.1–7.55 (m, 5 H). Anal. Calcd for C$_{13}$H$_{18}$O: C, 82.06; H, 9.53. Found: C, 82.01; H, 9.53.

To (*E*)-**55** (3.0 g, 15.8 mmol) was added 0.5 g of 85% phosphoric acid. After the mixture was heated at 80 °C for 2 h, it was partitioned between pentane and water. The pentane solutions were dried (MgSO$_4$) and concentrated to give 2.0 g (74%) of a product mixture which was separated by PGC (2.5 m Apiezon, 160 °C). 5-Methyl-4-phenyl-1,3-hexadiene (**56**, 18%): $^1$H NMR (CDCl$_3$) $\delta$ 1.05 (d, $J = 7$ Hz, 6 H), 2.7 (sept, $J = 7$ Hz, 1 H), 4.8–5.3 (m, 2 H), 5.95–6.3 (m, 2 H), 7.0–7.5 (m, 5 H). 2-Methyl-3-phenyl-2,4(*E*)-hexadiene (*E*-**36**, 26%): $^1$H NMR (CDCl$_3$) $\delta$ 1.55 (s, 3 H), 1.7 (dd, $J = 7$, 1 Hz, 3 H), 1.95 (s, 3 H), 5.0 (dq, $J = 16$, 7 Hz, 1 H), 6.65 (dq, $J = 16$, 1 Hz, 1 H), 7.0–7.5 (m, 5 H). Anal. Calcd for C$_{13}$H$_{16}$: C, 90.64; H, 9.36. Found: C, 90.53; H, 9.43. Data for 3-isopropyl-1-

methylindene (**57**, 56%) have been reported.[22] Analogous treatment of (*Z*)-**55** gave a similar product mixture; (*Z*)-**36** was not obtained.



**55**    **56**    *E*-**36**    **57**
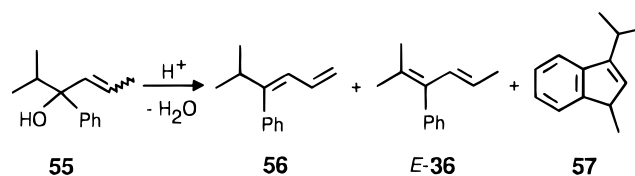
To a stirred, nitrogen-blanketed solution of 1-bromo-2-methyl-1-phenylpropene (**58**)[28] (4.0 g, 19 mmol) in ether (20 mL) was added at −78 °C *n*-butyllithium (1.6 M in ether, 40 mL, 64 mmol). After the mixture was allowed to warm to room temperature, stirring was continued for 5 h. A solution of *N*-formylpiperidine (2.5 g, 22 mmol) in ether (10 mL) was then added, and the reaction was allowed to proceed for 2 h at room temperature. The mixture was poured into ice water, and the phases were separated. The aqueous phase was extracted with ether (50 mL). The combined ether solutions were dried (MgSO$_4$) and concentrated in vacuo. Chromatography (silica gel, ether-hexane = 1:1) of the residue afforded 0.22 g (6.2%) of 2-methyl-3-phenyl-2-heptene (**59**): [$^1$H NMR (CDCl$_3$) $\delta$ 0.8–1.4 (m, 7 H), 1.6 (s, 3 H), 1.8 (s, 3 H), 2.3 (t, $J = 6$ Hz, 2 H), 7.0–7.4 (m, 5 H)] and 1.98 g (65%) of 3-methyl-2-phenyl-2-butenal (**60**) [IR (CDCl$_3$) 1670 cm$^{-1}$ (C=O); $^1$H NMR (CDCl$_3$) $\delta$ 1.8 (s, 3 H), 2.35 (s, 3 H), 6.9–7.1 (m, 2 H), 7.3–7.4 (m, 3 H), 10.25 (s, 1 H)].



**58**  X = Br
**59**  X = *n*-C$_4$H$_9$
**60**  X = CHO
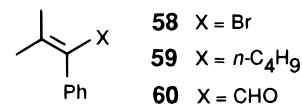
To a suspension of sodium amide (0.25 g, 6.2 mmol) in ether (20 mL) was added ethyltriphenylphosphonium iodide (2.5 g, 6.2 mmol). The mixture was heated at reflux for 24 h. A solution of **60** (0.5 g, 3.1 mmol) in ether (5 mL) was then added, and heating at reflux was continued for 2 h. The solution was filtered and concentrated in vacuo to give 0.4 g (75%) of **36**, $E{:}Z = 1{:}4$. The mixture was purified by PGC (1 m DC200, 140 °C), which did not separate the isomers. *Z*-**36**: $^1$H NMR (CDCl$_3$) $\delta$ 1.4 (dd, $J = 7$, 1.5 Hz, 3 H), 1.5 (s, 3 H), 1.7 (s, 3 H), 5.5 (dq, $J = 11$, 7 Hz, 1 H), 6.1 (dq, $J = 11$, 1.5 Hz, 1 H), 7.0–7.35 (m, 5 H). Anal. Calcd for C$_{13}$H$_{16}$: C, 90.64; H, 9.36. Found: C, 90.44; H, 9.24.

**1-Methyl-2-phenyl-1-(1-propenyl)cyclopropanes (37).** Using the same procedure for the synthesis of *trans*-1-methyl-2-phenylcyclopropanemethanol (*trans*-**50**),[24] ethyl *cis*-1-methyl-2-phenylcyclopropanecarboxylate[24b] was reduced to give 90% of *cis*-**50**: $^1$H NMR (CDCl$_3$) $\delta$ 0.7–1.2 (m, 2 H), 1.35 (s, 3 H), 2.05 (dd, $J = 9$, 7 Hz, 1 H), 3.25 (m, 2 H), 7.1–7.3 (m, 5 H). Following a method similar to the preparation of **53**, oxidation of the alcohols with MnO$_2$ (benzene, reflux) afforded the corresponding aldehydes (91–95%). *trans*-1-Methyl-2-phenylcyclopropanecarboxaldehyde (*trans*-**51**): IR (CDCl$_3$) 1690 cm$^{-1}$ (C=O); $^1$H NMR (CDCl$_3$) $\delta$ 0.95 (s, 3 H), 1.4–1.7 (m, 2 H), 2.55 (dd, $J = 9$, 7 Hz, 1 H), 7.1–7.3 (m, 5 H), 8.95 (s, 1 H). *cis*-1-Methyl-2-phenylcyclopropanecarboxaldehyde (*cis*-**51**):[29] IR (CDCl$_3$) 1690 cm$^{-1}$ (C=O); $^1$H NMR (CDCl$_3$) $\delta$ 1.35 (s, 3 H), 1.4–1.7 (m, 2 H), 2.55 (dd, $J = 9$, 7 Hz, 1 H), 7.1–7.3 (m, 5 H), 8.55 (s, 1 H). Wittig reaction of *trans*-**51** with ethyltriphenylphosphonium iodide–NaH–DMSO (see preparation of **54**) afforded predominantly (*E*:*Z* = 1.8, 75%) *trans*-1-methyl-2-phenyl-1-[(*E*)-1-propenyl]cyclopropane (*trans*-*E*-**37**); $^1$H NMR (CDCl$_3$) $\delta$ 0.95 (s, 3 H), 1.1 (d, $J = 7$ Hz, 2 H), 1.85 (d, $J = 5$ Hz, 3 H), 2.1 (t, $J = 7$ Hz, 1 H), 5.0–5.8 (m, 2 H), 7.1–7.4 (m, 5 H). The Wittig reaction of *trans*-**51** with ethyltriphenylphosphonium iodide–NaNH$_2$–ether (see preparation of *Z*-**36**) gave predominantly (*E*:*Z* = 0.2, 83%) *trans*-1-methyl-2-phenyl-1-[(*Z*)-1-propenyl]cyclopropane (*trans*-*Z*-**37**); $^1$H NMR (CDCl$_3$) $\delta$ 0.9 (s, 3 H), 1.0 (dd, $J = 6.5$, 3.5 Hz, 1 H), 1.05 (dd, $J = 8.5$, 3.5 Hz, 1 H), 1.8 (dd, $J = 7$, 1.5 Hz, 3 H), 2.1 (dd, $J = 8.5$, 6.5

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Hz, 1 H), 5.45 (dq, $J = 11, 7$ Hz, 1 H), 5.65 (dq, $J = 11, 1.5$ Hz, 1 H), 7.15−7.3 (m, 5 H). Anal. Calcd for $C_{13}H_{16}$: C, 90.64; H, 9.36. Found: C, 90.63; H, 9.37. Analogous reactions of *cis*-**51** afforded *cis*-*E*-**37** (*E:Z* = 5.0, 70%) and *cis*-*Z*-**37** (*E:Z* < 0.01, 75%), respectively. *cis*-*E*-**37**: $^1$H NMR (CDCl$_3$) $\delta$ 1.15 (d, $J = 7$ Hz, 2 H), 1.32 (s, 3 H), 1.67 (d, $J = 7$ Hz, 3 H), 1.95 (t, $J = 7$ Hz, 1 H), 5.0−5.7 (m, 2 H), 7.0−7.3 (m, 5 H). Anal. Calcd for $C_{13}H_{16}$: C, 90.64; H, 9.36. Found: C, 90.63; H, 9.44. *cis*-*Z*-**37**: $^1$H NMR (CDCl$_3$) $\delta$ 0.9−1.05 (m, 1 H), 1.1−1.2 (m, 1 H), 1.3 (s, 3 H), 1.65 (dd, $J = 7, 1.5$ Hz, 3 H), 1.9 (m, 1 H), 5.15 (dq, $J = 11, 1.5$ Hz, 1 H), 5.45 (dq, $J = 11, 7$ Hz, 1 H), 7.0−7.3 (m, 5 H).

**Reaction Products of 1-Phenyl-3-pentenylidene (42).** The tosylhydrazones *E*-**38** and *Z*-**38**[14] were converted into the sodium salts *E*-**39** and *Z*-**39**, respectively, according to the general procedure. The products obtained on pyrolysis and photolysis of **39** were analyzed by GC (60 m Marlophen, 130 °C); yields were estimated with 1-phenyl-2-butene as an internal standard (Tables 3 and 4). The pyrolysis mixtures were also separated by HPLC (Si-50-5-NO$_2$, hexane). Controls revealed *Z/E* isomerization of the dienes **44**−**46** on both direct and sensitized irradiation in diglyme. No significant isomerization occurred when the light was filtered with aqueous 0.1 M NaNO$_2$.

Samples obtained from stereoselective syntheses served to identify (*E*)-5-phenyl-2-pentene (*E*-**41**)[30,31] and *Z*-**41**.[31,32] Solutions of the diazo compounds **40** in methanol were treated with a few drops of methanolic HCl to give the ethers **43**, which were purified by HPLC (Si-60-5-C18, methanol−water = 3:1). 5-Methoxy-5-phenyl-(*E*)-2-pentene (*E*-**43**): $^1$H NMR (CDCl$_3$) $\delta$

1.55 (d, $J = 7$ Hz, 3 H), 2.25−2.5 (m, 2 H), 3.02 (s, 3 H), 4.05 (t, $J = 6.5$ Hz, 1 H), 5.3−5.5 (m, 2 H), 7.2−7.3 (m, 5 H). Anal. Calcd for $C_{12}H_{16}O$: C, 81.78; H, 9.15. Found: C, 81.66; H, 9.12. *Z*-**43**: $^1$H NMR (CDCl$_3$) $\delta$ 1.45 (d, $J = 7$ Hz, 3 H), 2.3−2.6 (m, 2 H), 3.2 (s, 3 H), 4.1 (t, $J = 7$ Hz, 1 H), 5.3−5.5 (m, 2 H), 7.2−7.3 (m, 5 H). Anal. Calcd for $C_{12}H_{16}O$: C, 81.78; H, 9.15. Found: C, 81.87; H, 9.12. Previous approaches led to **43** of unspecified configuration.[33]

The NMR spectra of (*E*)- and (*Z*)-2-phenyl-1,3-pentadiene (**44**) were in accordance with those reported.[34] The reaction of MeCH=CHCH=PPh$_3$ with benzaldehyde[35] afforded a mixture of 1-phenyl-1,3-pentadienes which was separated by PGC (4.5 m Apiezon, 150 °C). *E*-**45**: $^1$H NMR (CDCl$_3$) $\delta$ 1.85 (dd, $J = 7, 1$ Hz, 3 H), 5.85 (dq, $J = 15, 7$ Hz, 1 H), 6.2 (ddq, $J = 15, 11, 1$ Hz, 1 H), 6.4 (d, $J = 15.5$ Hz, 1 H), 6.75 (dd, $J = 15.5, 11$ Hz, 1 H), 7.2−7.4 (m, 5 H). *Z*-**45**: $^1$H NMR (CDCl$_3$) $\delta$ 1.9 (dd, $J = 7, 1.8$ Hz, 3 H), 5.6 (dq, $J = 10.5, 7$ Hz, 1 H), 6.2 (ddq, $J = 11, 10.5, 1.8$ Hz, 1 H), 6.5 (d, $J = 15.5$ Hz, 1 H), 7.1 (dd, $J = 15.5, 11$ Hz, 1 H), 7.2−7.4 (m, 5 H). *E*-**46**: $^1$H NMR (CDCl$_3$) $\delta$ 1.75 (d, $J = 6.5$ Hz, 3 H), 5.85 (dq, $J = 15, 6.5$ Hz, 1 H), 6.15 (t, $J = 11$ Hz, 1 H), 6.25 (d, $J = 11$ Hz, 1 H), 6.4−6.75 (m, 1 H), 7.2−7.5 (m, 5 H). *Z*-**46**: $^1$H NMR (CDCl$_3$) $\delta$ 1.85 (d, $J = 7$ Hz, 3 H), 5.65 (dq, $J = 10, 7$ Hz, 1 H), 6.4−6.6 (m, 3 H), 7.2−7.35 (m, 5 H). Low-resolution NMR spectra have previously been reported for *E*-**45** and *E*-**46**.[36]

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