mechanisms (Rideal-type processes[14a]) and diffusion of the reactants on the surface (Langmuir–Hinschelwood-type processes).[14b] The complexiity of mechanisms between these two extremes may be substantial, especially with geometrically and energetically heterogeneous surfaces where reaction pathways are not necessarily associated with pure gas-phase bombardment or with pure surface diffusion, i.e., molecular motions can be a combination of both, involving jumps from wall to wall and from one crest to another. It seems to us, however, that a pure gas-phase bombardment mechanism can be excluded, even at this early stage. Thus, the number of collisions of gaseous molecules per unit time and unit surface of a spherical pore is only a function of pressure and not of pore diameter; i.e., a bombardment mechanism will not exhibit a dependence on pore size. (We note that the pore system in silica is open and interconnected, allowing for efficient O_2 equilibration between pores during the 10^{-6}–10^{-7}-s lifetime of the excited adsorbate). This conclusion is in keeping with that of Gafney et al., who excluded gas-phase bombardment in the case of quenching of $Ru(bpy)_3^{2+}$ on vycor glasses by O_2, SO_2, and NO_2.[15]

At present, we thus tend to favor the alternative explanation, based on a nonhomogeneous coadsorption quenching mechanism according to the following considerations: At low θ values both probe and O_2 will be preferentially adsorbed on surface zones which originate in the low-diameter tail of the pore-size distribution curve. this is not only due to energetic factors (the number of adsorption sites/unit area in small, concave pores is higher than the average) but also due to the simple fact that most of the surface area is concentrated in narrow pores.[16] Thus, in narrow pores the equilibrium

$$O_2(\text{molecules/unit area}) \rightleftharpoons O_2(\text{gas phase})$$
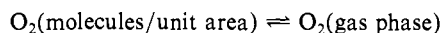
is shifted to the left relative to wide pores, resulting in a higher local oxygen concentration. Consequently, a higher quenching efficiency via a short-range surface diffusion mechanism is observed. In larger aps silicas, where the relative amount of narrow pores decreases, long-range (surface) diffusion pathways, as well as gas-phase collisions, may prevail, leading to diminished quenching rates.

Preliminary O_2 quenching experiments were also carried out with some other silicas with varying psd. A general behavior similar to that of Si-60 was observed in the case of Merck Si-200 and Si-500 while Si-2500 exhibited O_2-quenching efficiencies similar to Si-1000.

Finally, it should be noted that a number of investigators have observed profound differences between solution and surface quenching behavior of excited singlet and triplet state by gaseous quenchers.[17] It cannot be excluded that in some of these systems the enhanced quenching process may be attributed to high local quencher concentrations associated with surface geometry features, e.g., trapping in very narrow pores. Similarly, Casal and Scaiano[18] have observed deviations from Stern–Volmer plots in the O_2 quenching of triplet ketones adsorbed on silicalite. They interpreted their observations as due to site inhomogeneities in this zeolite. Again, it is plausible that these inhomogeneities are associated with geometrical factors such as zeolitic structural imperfections.

Further work (e.g., dependence on O_2 pressure, probe concentration, presence of coadsorbates) is in progress in our laboratory aiming at obtaining a quantitative model for the struc-

ture-sensitive catalytic effect reported here.

Stereocontrolled [m + n] Annulation Reactions. 2. A [3 + 3] Route to Chiral, Nonracemic 1,2-Cyclohexanediols

Gary A. Molander* and David C. Shubert[1]

*Department of Chemistry and Biochemistry
University of Colorado, Boulder, Colorado 80309-0215*

Received September 9, 1986

As part of an ongoing program initiated to generate stereocontrolled approaches to a variety of carbocyclic ring systems,[2] we sought to develop a [3 + 3] annulation strategy utilizing three carbon dielectrophilic synthons in conjunction with 3-iodo-2-[(trimethylsilyl)methyl]propene[3]/SnF_2[4] as a trimethylenemethane dianionic synthon. Few [3 + 3] approaches to six-membered rings utilizing dianion/dielectrophile strategies have been reported.[5] While highly effective in generating functionalized ring systems, existing approaches do not address the important problems of controlling relative and absolute stereochemistry in construction of functionalized carbocycles.

We sought strategies that would allow control of stereochemistry at several stereocenters and, furthermore, permit straightforward generation of chiral, nonracemic cyclization products. Efforts therefore focused on use of α,β-epoxy aldehydes as the dielectrophilic partner in the [3 + 3] process. Epoxy aldehydes are extremely attractive substrates since they are readily accessible in high enantiomeric excess from appropriate allylic alcohols by Sharpless asymmetric epoxidation[6] followed by Swern oxidation[7] of the resulting epoxy alcohols, as well as by other techniques.[8]

In the [3 + 3] annulation process envisioned, addition of allyltin trihalide (generated in situ) to the carbonyl of the epoxy aldehyde was expected to occur with good diastereofacial selectivity in the Felkin–Ahn sense as reported previously for a number of related substrates.[4c,f] The combination of intramolecular Sn^{4+} Lewis acid

(1) National Science Foundation Predoctoral Fellow, 1984–1987.

(2) (a) Molander, G. A.; Etter, J. B. *J. Org. Chem.* **1986**, *51*, 1778. (b) Molander, G. A.; Andrews, S. W. *Tetrahedron Lett.* **1986**, *27*, 3115. (c) Molander, G. A.; Shubert, D. C. *J. Am. Chem. Soc.* **1986**, *108*, 4683. (d) Molander, G. A.; Etter, J. B.; Zinke, P. W. *J. Am. Chem. Soc.*, in press.

(3) This reagent and congeners have been utilized as dipolar synthons for annulation reactions. (a) Trost, B. M.; Vincent, J. E. *J. Am. Chem. Soc.* **1980**, *102*, 5680. (b) Knapp, S.; O'Connor, U.; Mobilio, D. *Tetrahedron Lett.* **1980**, 4557. (c) Trost, B. M.; Curran, D. P. *J. Am. Chem. Soc.* **1981**, *103*, 7380. (d) Trost, B. M.; Chan, D. M. T.; Nanninga, T. N. *Org. Synth.* **1984**, *62*, 58.

(4) (a) Gambaro, A.; Peruzzo, V.; Plazzogna, G.; Tagliavini, G. *J. Organomet. Chem.* **1980**, *197*, 45. (b) Mukaiyama, T.; Harada, T.; Shoda, S. *Chem. Lett.* **1980**, 1507. (c) Harada, T.; Mukaiyama, T. *Chem. Lett.* **1981**, 1109. (d) Nagaoka, H.; Kishi, Y. *Tetrahedron* **1981**, *37*, 3873. (e) Mukaiyama, T.; Harada, T. *Chem. Lett.* **1981**, 621. (f) Mukaiyama, T.; Suzuki, K.; Yamada, T. *Chem. Lett.* **1982**, 929. (g) Auge, J.; David, S. *Tetrahedron Lett.* **1983**, *24*, 4009. (h) Auge, J. *Tetrahedron Lett.* **1985**, *26*, 753.

(5) (a) Bilyard, K. G.; Garratt, P. J.; Underwood, A. J.; Zahler, R. *Tetrahedron Lett.* **1979**, 1815. (b) Bilyard, K. G.; Garratt, P. J.; Zahler, R. *Synthesis* **1980**, 389. (c) Bilyard, K. G.; Garratt, P. J. *Tetrahedron Lett.* **1981**, *22*, 1755.

(6) (a) Katsuki, T.; Sharpless, K. B. *J. Am. Chem. Soc.* **1980**, *102*, 5974. (b) Rossiter, B. E.; Katsuki, T.; Sharpless, K. B. *J. Am. Chem. Soc.* **1981**, *103*, 464. (c) Martin, V. S.; Woodard, S. S.; Katsuki, T.; Yamada, Y.; Ikeda, M.; Sharpless, K. B. *J. Am. Chem. Soc.* **1981**, *103*, 6237. (d) Pfenninger, A. *Synthesis* **1986**, 89. (e) Hanson, R. M.; Sharpless, K. B. *J. Org. Chem.* **1986**, *51*, 1922.

(7) Mancuso, A. J.; Swern, D. *Synthesis* **1981**, 165.

(8) (a) Adam, W.; Griesbeck, A.; Staab, E. *Tetrahedron Lett.* **1986**, *27*, 2839. (b) Hayashi, M.; Terashima, S.; Koga, K. *Tetrahedron* **1981**, *37*, 2797. (c) Abdel-Magid, A.; Pridgen, L. N.; Eggleston, D. S.; Lantos, I. *J. Am. Chem. Soc.* **1986**, *108*, 4595.

(14) (a) Adamson, A. W. *Physical Chemistry of Surfaces*; 4th ed.; Wiley: New York, 1982; p 628. (b) *Ibid*, p 631.

(15) Wolfgang, S.; Gafney, H. D. *J. Phys. Chem.* **1983**, *87*, 5395.

(16) Shields, J. E.; Lowell, S. *Powder Technol.* **1983**, *36*, 1.

(17) Turro, N. J.; Gould, I. R.; Zimmt, M. B.; Cheng, C.-C. *Chem. Phys. Lett.* **1985**, *119*, 484. Beck, G.; Thomas, J. K. *Ibid.* **1983**, *94*, 553.

(18) Casal, H. L.; Scaiano, J. C. *Can. J. Chem.* **1984**, *62*, 628; **1985**, *63*, 1308.

(19) Wellner, E.; Ottolenghi, M.; Avnir, D.; Huppert, D. *Langmuir* **1986**, *2*, 616.

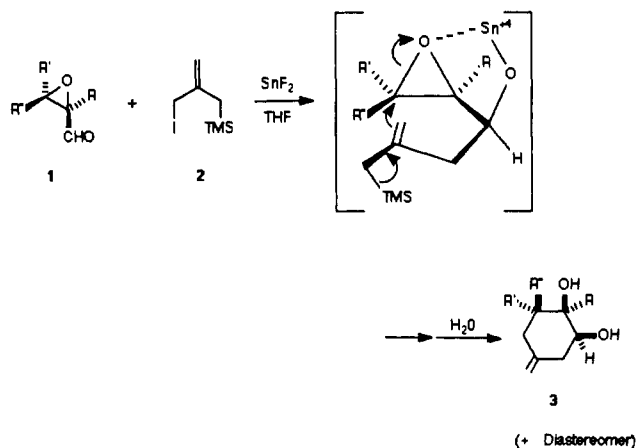(20) Huppert, D.; Kanety, H.; Kosower, E. W. *Chem. Phys. Lett.* **1981**, *84*, 48.

Communications to the Editor

J. Am. Chem. Soc., Vol. 109, No. 2, 1987 577

Figure 1.

Table I. [3 + 3]Annulation Utilizing α,β-Epoxy Aldehydes (1) in Reaction with 3-Iodo-2-[(trimethylsilyl)methyl]propene (2) and Stannous Fluoride

entry	R	R'	R''	% isolated yield[a]	diastereomer ratio[b]
1	n-Bu	H	H	67	50:1
2	n-Pr	n-Pr	H	67	50:1
3	H	-(CH₂)₄-		59	4:1
4	H	n-C₈H₁₇	H	53	4.9:1
5	Et	H	Et	37[c]	19:1
6	-(CH₂)₄-		H	19	6.9:1
7	Et	Et	Et	19	6:1
8	H	H	n-C₈H₁₇	0	-

[a] Refers to yield of one pure diastereomer as determined by capillary GC analysis and all spectral data. [b] Minimum diastereoselectivity as determined by capillary GC analysis of crude reaction mixtures. [c] Contaminated with an inseparable, unknown impurity.

catalysis and fluoride-induced nucleophilic assistance was anticipated to facilitate epoxide ring opening by the intermediate allylsilane. It was predicted that the presence of a "localized" Lewis acid would preferentially polarize the carbon–oxygen bond of the epoxide distal to the inductively electron-withdrawing alkoxide oxygen in the intermediate,[9] inducing spontaneous allylsilane reaction at that site, generating a six-membered ring (Figure 1). It was hoped that rapid cyclization would occur to ensure strict inversion of configuration at the epoxide,[10] thereby establishing good diastereoselectivity at three contiguous stereocenters on the newly formed ring.

Epoxy aldehydes ultimately derived from nerol and geraniol were initially utilized to examine the effectiveness of the procedure. Treatment of these substrates with 2 and SnF₂ in THF led to isolation of the expected products in 50% isolated yields (eq 1 and 2), with no intermediates detected at any time during the course of the reaction.
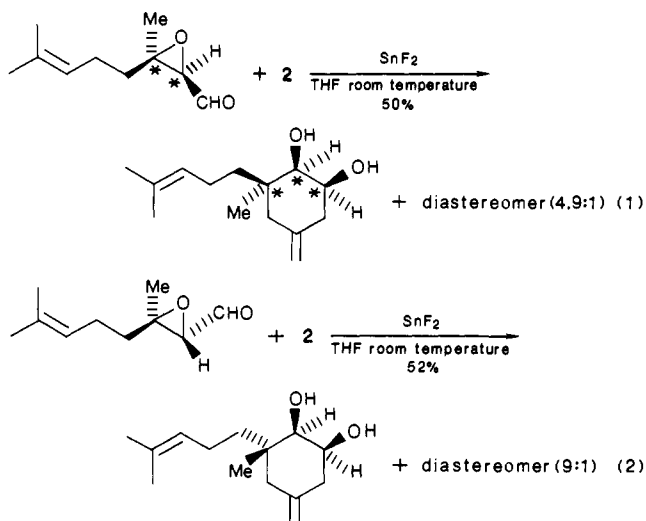
That the cis diol was generated as the major isomer in each case was confirmed by 200-MHz ¹H NMR analysis of the acetonide derived from each major diol diastereomer. Coupling constants between the two bridgehead methine protons were 4.6 and 4.9 Hz, respectively, in the two derivatives, clearly indicative of an axial–equatorial relationship between these protons. The corresponding coupling constant for the acetonide of the minor diastereomer from the nerol-derived substrate (epimeric due to opposite diastereofacial addition to the aldehyde) was 9.1 Hz.

Generation of chiral, nonracemic materials has been demonstrated utilizing the epoxy aldehyde ultimately derived from nerol

(eq 1), employing Sharpless asymmetric epoxidation conditions [Ti(O-i-Pr)₄/L-(+)-diethyl tartrate/t-BuOOH, 80% ee[11]], followed by Swern oxidation. The resulting cyclohexanediol was obtained with complete retention of absolute stereochemistry (80% ee).[12]

A variety of substitution patterns about the epoxide can be tolerated by the reaction, in some cases with excellent diastereoselectivity and yields (Table I). Thus, carbonyl addition to the aldehyde followed by cyclization onto epoxides unsubstituted at the reaction site (entry 1), as well as those monosubstituted (entries 2 and 4) and disubstituted at the epoxide centers (entry 3), have all been established. The reaction is not yet completely general, however (entries 5–8). We have found some of these epoxy aldehydes to be extremely sensitive, undergoing noticeable polymerization on standing at low temperatures. Substrates which are somewhat more highly hindered about the aldehyde undoubtedly undergo slower carbonyl addition, and the Sn⁴⁺ species generated in the process may polymerize the unreacted epoxy aldehyde substrate. Alternatively, cyclization in these substrates may be inhibited, again leading to polymeric products. Procedures designed to eliminate this problem are currently under investigation.

No [3 + 2] annulation products have been observed in any reactions performed to date. Even in an instance where stereoelectronic factors would seem to favor a [3 + 2] process, only [3 + 3] products are observed.[13] Thus, there is a well-known

9:1 mixture of diastereomers
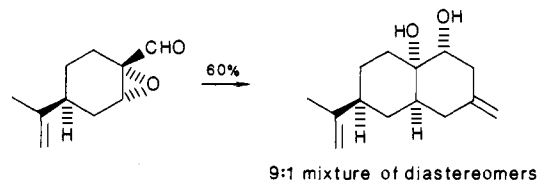
tendency for cyclohexene oxides to undergo reaction such that the incoming nucleophile and resulting hydroxyl group have a trans-diaxial relationship with one another.[14] In the above example, the isopropenyl group is expected to anchor the substrate into a single conformation. Under these circumstances, the intermediate allylsilane generated by reaction of allyltin trihalide with the aldehyde might be expected to undergo axial attack at the proximal position of the epoxide, generating a spirocyclic diol. In fact, the tendency for epoxide ring opening at the site distal to the alkoxide[9] generated in these processes clearly overrides this

(9) (a) Caron, M.; Sharpless, K. B. *J. Org. Chem.* **1985**, *50*, 1557. (b) Chong, J. M.; Sharpless, K. B. *J. Org. Chem.* **1985**, *50*, 1560.

(10) Parker, R. E.; Isaacs, N. S. *Chem. Rev.* **1959**, *59*, 737.

(11) Determined by ¹H NMR of the corresponding acetate with Eu(hfc)₃ as a chiral shift reagent. Hill, J. G.; Sharpless, K. B. *Org. Synth.* **1985**, *63*, 66.

(12) Material of relatively low enantiomeric excess was utilized to facilitate determination of enantiomeric excess by ¹H NMR with Eu(hfc)₃ as a chiral shift reagent.

(13) Stereochemistry of the major diastereomer was determined by obtaining a crystal structure of the diol diketone derived from the product by ozonolysis.

(14) (a) Barton, D. H. R.; Cookson, R. C. *Q. Rev. Chem. Soc.* **1956**, *10*, 44. (b) Eliel, E. L. In *Steric Effects in Organic Chemistry*; Newman, M. S., Ed.; Wiley: New York, 1956; pp 130–134. (c) Eliel, E. L. *Stereochemistry of Carbon Compounds*; McGraw-Hill: New York, 1962; pp 229–231.

normally preferred reactivity pattern.

The [3 + 3] annulation strategy described herein represents a promising new approach to highly functionalized six-membered ring carbocycles. Good to excellent stereochemical control can be achieved at multiple stereocenters in a predictable fashion, and products can be readily accessed in chiral, nonracemic form.

Supplementary Material Available: General synthetic procedure and complete spectral data for all compounds synthesized (8 pages). Ordering information is given on any current masthead page.

Formation of 2,3-Dehydro-1,2-dihydro-1,1-dimethylnaphthalene, an "Isoaromatic" Molecule

Bernard Miller* and Xiaolian Shi[†]

Department of Chemistry, University of Massachusetts
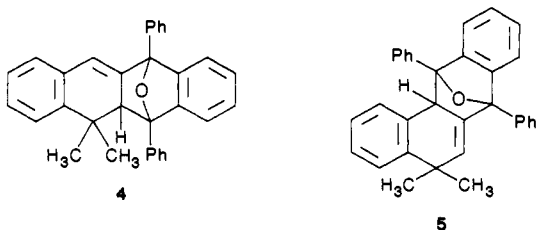*Amherst, Massachusetts 01003*

Compounds containing 1,3,5-cyclohexatriene rings ("aromatic compounds") are well-known. In contrast, compounds containing 1,2,4-cyclohexatriene rings ("isoaromatic compounds") have never previously been observed even as transient intermediates.

We now report evidence for the formation and trapping of 2,3-dehydro-1,2-dihydro-1,1-dimethylnaphthalene (1), the first example of a molecule containing a 1,2,4-cyclohexatriene ring.

1
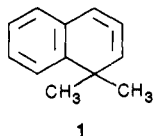
Hydrocarbon 1 was formed by dehydrobromination of 2 (or its isomer 3).[1] Bromo olefins 2 and 3 were prepared in ca. 3:1 ratio from 1,1-dimethyl-2-tetralone as shown in Scheme I. The major isomer, 2, could be rapidly and quantitatively converted to 3 by treatment with potassium *tert*-butoxide solutions at room temperature (Scheme I).
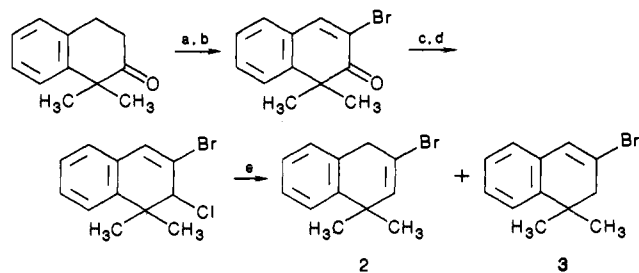
When potassium *tert*-butoxide was added to a THF solution containing equimolar amounts of 2 and 1,3-diphenylisobenzofuran at 50 °C, adducts 4 (mp 192–194 °C) and 5 (mp 171–173 °C) were obtained in a 3:2 ratio. (After chromatography on silica gel, the combined yield of 4 and 5 was 20%.) The structures of the two adducts were demonstrated by their elemental analyses and spectra.[2]

4

5

Scheme I[a]

2   **3**

[a] (a) 2Br$_2$; (b) quinoline, 120 °C; (c) NaBH$_4$, CeCl$_3$; (d) HCl, CH$_2$Cl$_2$, 0 °C; (e) NaBH$_4$ in aqueous diglyme.

Formation of adducts 4 and 5 can only reasonably result from Diels–Alder condensation reactions of the reactive intermediate 1.

Reaction of either 2 or 3 with potassium *tert*-butoxide at 50 °C in the absence of 1,3-diphenylisobenzofuran yielded, in addition to a mixture of hydrocarbons from which no single compound could be isolated, the vinyl ether 6, identified by its elemental

6   **7**
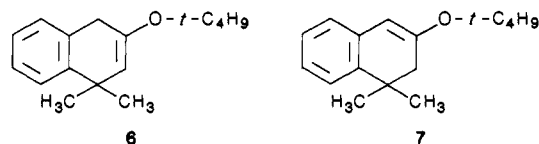
analysis and spectra[3] and its conversion to 3,3-dimethyl-2-tetralone on reaction with dilute acid. (Ether 6 can also be isolated in small amounts from reaction mixtures including 1,3-diphenyliso-benzofuran.)

Most of the plausible routes for displacement of bromide in reaction of 2 or 3 with potassium *tert*-butoxide (e.g., addition-elimination of *tert*-butoxide to 3 or initial dehydrobromination of 3 to form a benzocyclohexyne) should yield the conjugated ether 7 rather than 6.[4] However, no evidence for formation of 7 could be detected. It is improbable that 7 would isomerize completely to 6 under the reaction conditions, since 7 should be the more stable isomer[5] and since we observed that 2-methoxy-1,4-dihydronaphthalene does not undergo isomerization to its conjugated isomer even at much longer reaction times under similar reaction conditions. We therefore suggest that 6 is formed by reaction of potassium *tert*-butoxide with 1, with the resulting anion undergoing kinetically controlled protonation at the central carbon:
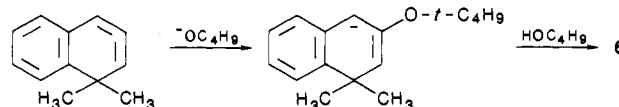
(2) Compound 4: ^{1}H NMR (300 MHz) δ 0.18 (s, 3 H), 1.44 (s, 3 H), 3.76 (d, J = 2.7 Hz, 1 H), 6.52 (d, J = 2.7 Hz, 1 H), 7.06–7.26 (m, 6 H), 7.39–7.55 (m, 7 H), 7.65 (d, J = 7.7, 1 H), 7.86 (d, J = 7.3, 2 H), 7.97 (d, J = 9.0, 2 H); ^{13}C NMR δ 22.72, 26.35, 38.32, 55.60, 88.86, 90.81, 116.98, 119.64, 122.56, 123.92, 125.97, 126.19, 127.06, 127.22, 127.44, 127.65, 128.30, 128.52, 128.68, 133.61, 135.02, 136.75, 144.77, 145.48, 145.75, 147.26. Anal. C, H. Compound 5: ^{1}H NMR δ 1.36 (s, 3 H), 1.43 (s, 3 H), 4.65 (d, J = 2.7 Hz, 1 H), 5.85 (d, J = 2.7 Hz, 1 H), 1.04–1.25 (m, 7 H), 7.43–7.55 (m, 7 H), 7.82–7.95 (m, 4 H); ^{13}C NMR δ 28.89, 29.49, 38.75, 47.48, 89.51, 90.98, 118.49, 123.16, 123.75, 125.00, 125.76, 125.97, 126.24, 127.11, 128.14, 128.57, 129.28, 129.93, 134.91, 135.43, 135.75, 144.77, 144.18, 147.32.

(3) ^{1}H NMR δ 1.26 (s, 6 H), 1.43 (s, 9 H), 2.22 (d, J = 1.3 Hz, 2 H), 5.28 (t, J = 1.3 Hz, 1 H), 6.9–7.3 (m, 4 H). Anal. C, H.

(4) Formation of an ether from 2 rather than 3 seems unlikely, both because of the very low concentration of 2 in equilibrium with 3 and because both addition of bases to 2 and elimination of HBr from 2 should be much slower than similar reactions of 3.

(5) 1-Methoxy-1,3-cyclohexadiene has been shown to be the most stable of the methoxycyclohexadiene isomers (Taskinnen, E.; Nummelin, K. J. Org. Chem. 1985, 50, 4844).

[†] Visiting scholar from Zhejiang University, Hangzhou, PRC.
(1) 1,2-Cyclohexadienes have similarly been prepared by dehydrobromination of 1-bromocyclohexenes: Wittig, G.; Fritze, P. Justus Liebigs Ann. Chem. 1968, 711, 82. Bottini, A. T.; Corson, F. P.; Fitzgerald, R.; Frost, K. A., II. Tetrahedron 1972, 28, 4881. Bottini, A. T.; Hilton, L. L.; Plott, J. Ibid. 1975, 31, 1997. Balci, M.; Jones, W. M. J. Am. Chem. Soc. 1980, 102, 7607; 1981, 103, 2874.