suggests that the leaving group "sees" a larger negative charge development from the attack of the anion in the transition state for weakly basic compared with strongly basic nucleophiles. The change depends on the basicity rather than the reactivity of the nucleophile, as shown by the change in slope for acetohydroxamate anion, and may be influenced by the class of nucleophile, because all of the compounds of $pK \leq 10$ are secondary or tertiary alcohols except for the acetohydroxamate anion. The change in slope corresponds to a change in the value of β_{lg} from −0.3 to −0.4 for the weakly basic nucleophiles.

This change probably represents a small change in transition-state structure, with a larger amount of bond formation for the less basic nucleophiles. There is evidence consistent with a similar change for the attack of thiol anions on acetaldehyde.[50] However, the change in β_{lg} from −0.3 to −0.4 for attack of oxygen anions on esters is much smaller than the change in β_{nuc} from 0.7 to 0.2–0.3 with increasing pK of the nucleophile (Figure 2).[51] This disparity in the changes of β_{nuc} and β_{lg} provides additional evidence that factors other than changes in transition-state structure are required to account for the curvature of the Brønsted plot in Figure 2.

This conclusion is consistent with the observation that there is little or no change in the secondary α or β deuterium isotope effects for rate-determining nucleophilic attack of oxygen anions on formate or acetate esters with changing basicity of the nucleophile or leaving group.[7,52] In particular, the secondary α-deuterium isotope effect of $k_D/k_H = 1.22$ for the attack of a series of phenolate and alkoxide ions on p-nitrophenyl formate is large and constant, suggesting that there is a considerable amount of bond formation and little change in the structure of the transition states for these nucleophiles.[53] Similarly, the p_{xy} coefficient for deprotonation of a series of (2-(p-nitrophenyl)ethyl)quinuclidinium ions is indistinguishable from zero, although the large curvature of the Brønsted plot corresponds to a value of $p_x = 0.07$.[18]

This work provides additional support for the conclusions (1) that observed β values for basic oxygen anions do not provide a reliable measure of the amount of bond formation or cleavage in the transition state[44] and (2) that curved structure–reactivity plots for reactions involving these anions do not necessarily represent changes in transition-state structure.[5,6,49]

Registry No. D_2O, 7789-20-0; $(CF_3)_2(OH)_2$, 677-71-4; $(CHF_2)_2C(OH)_2$, 918-45-6; $(CF_3)_2CHOH$, 920-66-1; $CH_3(CF_3)C(OH)_2$, 421-76-1; $(CF_3)_3COH$, 2378-02-1; p-nitrophenyl acetate, 830-03-5; 2,4-dinitrophenyl acetate, 4232-27-3; 1-acetoxy-4-methoxypyridinium ion, 46123-02-8; 1-acetoxy-4-methoxypyridinium perchlorate, 19921-03-0.

(50) Gilbert, H. F.; Jencks, W. P. *J. Am. Chem. Soc.* **1977**, *99*, 7931–7947.
(51) The limiting magnitudes of β_{nuc} and β_{lg} for formation of an anionic addition intermediate are expected to be similar: the limiting values of β_{nuc} and β_{lg} are approximately 0.8 and −0.9, respectively, from a value of $\beta_{nuc} = 1.0$ and $\beta_{lg} = -0.7$ for the formation of an uncharged intermediate[47] and a correction of −0.2 for the negative charge of an anionic intermediate (Sayer, J. M.; Jencks, W. P. *J. Am. Chem. Soc.* **1973**, *95*, 5637–5649).
(52) do Amaral, L.; Bastos, M. P.; Bull, H. G.; Ortiz, J. J.; Cordes, E. H. *J. Am. Chem. Soc.* **1979**, *101*, 169–173.
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Conversion of Allyl Alcohols to 1,3-Dienes by Sequential Sulfenate–Sulfoxide [2,3] Sigmatropic Rearrangement and Syn Elimination[1]

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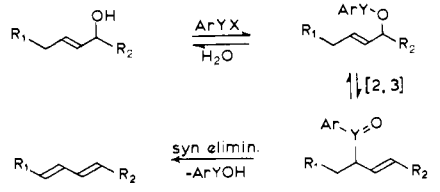
Abstract: A method for the 1,4 dehydration of allyl alcohols to give 1,3-dienes has been developed. The technique involves treatment of the allyl alcohol with 2,4-dinitrobenzenesulfenyl chloride and triethylamine. The sulfenate ester so formed undergoes [2,3] sigmatropic rearrangement to the isomeric allylic sulfoxide, followed by thermal syn elimination to give a diene. A number of different systems were studied to establish the conditions needed for successful reaction, tolerance to various substitution patterns, regiospecificity, the stereochemistry of the double bonds formed, and the side reactions that occur. Successful reactions were carried out with allyl alcohols having alkyl, phenyl, furyl, sulfide, dithiane, sulfone, halide, and acetoxy substituents. The 1,4 dehydration was shown to occur with overall cis stereochemistry in a cyclic system, consistent with the postulated mechanism. The dehydration can also be performed with selenenyl halides, but conditions are more severe, and the reaction is less general than with 2,4-dinitrobenzenesulfenyl chloride.

The dehydration of allyl alcohols to dienes has been a reaction of limited general utility because yields are often modest and both 1,2 and 1,4 eliminations are observed under typical dehydration conditions.[3] In addition to treatment with catalytic amounts of sulfonic acids, Burgess reagent,[3a] pyrolysis over alumina,[3b] acetate pyrolysis,[3c,d] and other standard olefin dehydration procedures, allyl alcohols have been dehydrated by treatment of the derived acetates with Pd(II) salts[3e] and by a multistep sequence involving epoxidation, base-catalyzed elimination, and reductive elimination.[4]

Scheme I



(1) Preliminary communication: Reich, H. J.; Reich, I. L.; Wollowitz, S. *J. Am. Chem. Soc.* **1978**, *100*, 5981.
(2) These results were taken from the Ph.D. Thesis of S. Wollowitz, University of Wisconsin–Madison, 1980.
(3) (a) Burgess, E. M.; Penton, H. R., Jr.; Taylor, E. A. *J. Am. Chem. Soc.* **1970**, *92*, 5224. Paquette, L. A.; Henzel, R. P.; Wilson, S. E. *Ibid.* **1972**, *94*, 7780. (b) Corey, E. J.; Hortmann, A. G. *Ibid.* **1963**, *85*, 4034; **1965**, *87*, 5736. Hortmann, A. G.; Daniel, D. S.; Martinelli, J. E. *J. Org. Chem.* **1973**, *38*, 728. (c) Hill, R. K.; Bock, M. G. *J. Am. Chem. Soc.* **1978**, *100*, 637. (d) McCurry, P. M., Jr.; Abe, K. *Ibid.* **1973**, *95*, 5824. (e) Tsuji, J.; Yamakawa, T.; Kaito, M.; Mandai, T. *Tetrahedron Lett.* **1978**, 2075. Trost, B. M.; Verhoeven, T. R.; Fortunak, J. M. *Ibid.* **1979**, 2301.
(4) Yasuda, A.; Tanaka, S.; Yamamoto, H.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 1752.

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Only the last of these is specifically a 1,4-dehydration procedure.

An alternative to a direct dehydration would be a regiospecific transformation of the of the alcohol to some functionality that can undergo a pericyclic syn elimination. Specifically, we envisaged a reaction sequence as depicted in Scheme I, which utilizes a reversible [2,3] sigmatropic rearrangement to perform the required allylic transposition and the well-studied syn elimination of sulfoxides and selenoxides to form the double bond.

A particularly attractive aspect of Scheme I is that both the starting reagent (ArYX) and the product (ArYOH) are sulfenic or selenenic acid derived, and hence the transformation is potentially catalytic in ArYX, provided some in situ method of converting ArYOH back to ArYX can be found. Unfortunately, our work along these lines has so far been largely unsuccessful, although the stoichiometric reaction, as we will describe below, does work well.

The preparation and chemistry of allylic sulfenates and sulfoxides have been elegantly elucidated in studies by Mislow and co-workers.[5] The sulfoxide is usually thermodynamically favored in the [2,3] sigmatropic equilibrium, although the presence of low concentrations of sulfenate can be demonstrated by suitable trapping experiments.[6] Numerous synthetic applications of these rearrangements have been reported.[6,7] However, until the time this investigation was begun, there were no reports in the literature of syn eliminations of allyl sulfoxides to form 1,3-dienes regiospecifically.[8] In fact, both α-methylallyl[9] and α,α-dimethylallyl[6] sulfoxides have been reported to undergo a [1,3] sigmatropic shift in preference to syn elimination.[10] It is for this reason and the fact that selenoxide syn eliminations proceed at approximately 100 °C lower temperature than those of sulfoxides that we began our work by investigating the applicability of Scheme I with Y = Se.

The chemistry and thermodynamics of allylic selenoxides and their [2,3] sigmatropic rearrangement products, the allylic selenenates, are much less well studied than the sulfur analogues. Allylic selenoxides are generally unstable even well below room temperature,[11,12] and the intermediacy of the allyl selenenate esters could only be inferred because the alcohols are the products isolated even with no trapping agent other than adventitious moisture to cleave the selenenate ester. In fact, we have used the conversion of allyl selenides to allyl alcohols[11b] for the preparation of several of the starting materials used in the present study. The [2,3] sigmatropic rearrangement should, in analogy with the sulfur system, be reversible, but this had not been demonstrated when we began our work.

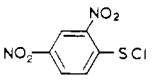
There have been several examples of allyl and propargyl selenoxides that undergo syn elimination in competition with [2,3] sigmatropic rearrangement.[11b,c,12a,b,13] In each case some feature of the system either retards the rearrangement or promotes the syn elimination.

The major unanswered questions relevant to the implementation of Scheme I (where Y = Se) as a diene synthesis are whether allylic selenenates can be prepared and whether they rearrange to selenoxides. The only known selenenate esters are those of *o*-nitrobenzeneselenenic and 1-anthraquinoneselenenic acids.[14]

Thus, with the above information in hand, we investigated the potential of sulfur and selenium reagents for the regiospecific dehydration of allyl alcohols. Herein is a full report of our work.[1]

Results and Discussion

We began our investigation by treating 1-(*o*-tolyl)-2-cyclohexenol (**1a**) with a series of selenenyl and sulfenyl halides. 2-Nitro-4-methylbenzeneselenenyl chloride was successful in converting **1a** to the diene **2a** via the corresponding selenenate ester in 65% yield. However, the reaction could not be generalized, and we eventually found that the commercially available 2,4-dinitrobenzenesulfenyl chloride (**3**) was the reagent of choice, being



3

both more readily available and reacting at lower temperature and in higher yield than *o*-nitrobenzeneselenenyl chloride. Diene **2a** was formed in a few minutes, with no contamination from other regioisomers. Our results with the selenium reagents are described later in this paper; first, we summarize the preparation of the required allyl alcohols and then discuss our extended findings on the 1,4 dehydration using 2,4-dinitrobenzenesulfenyl chloride.

Preparation of Allyl Alcohols. The allyl alcohols used in this study are presented in Table I. They were prepared by using the following procedures: (a) addition of organometallic reagents to α,β-unsaturated ketones and aldehydes—the organometallic reagents used (compound formed) are phenyllithium (**1c**, **4**, **9**, **14**, **42a**, **43a**), *o*-tolyllithium (**1a**), 2,5-dichlorophenyllithium (**1b**, **42b**, **43b**), decynyllithium (**13**), 1-propenylmagnesium bromide (**12**), (phenylsulfonyl)methyllithium (**18**), (phenylthio)methyllithium[15a] (**19**), α-(methylthio)benzyllithium[15b] (**40**), 2-lithiodithiane (**20**, **39**),[15c] and 2-(2-furyl)-2-lithiodithiane (**21**);[12b,15d] (b) alkylation or hydroxyalkylation of a metallated allylphenyl selenide, followed by oxidation of the selenide (**10**, **17**);[11b] (c) reaction of α-lithoalkyl phenyl selenoxides with aldehydes, followed by selenoxide syn elimination (**11**, **12**);[16] (d) acid-catalyzed allylic rearrangement of allyl alcohols (**5a**, **5b**); (e) reduction of α,β-unsaturated ketones (**6**, **8**); (f) miscellaneous transformations of allyl alcohols (**15**, **16**, **41**); (g) allylic oxidation (**7**).

1,4 Dehydrations of Allyl Alcohols. To test the scope of the preparation of dienes according to the method of Scheme I using

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(8) Several examples have been reported since (two using our procedure): (a) Isobe, H.; Iio, H.; Kitamura, M.; Goto, T. *Chem. Lett.* **1978**, 541. (b) Blatcher, P.; Grayson, J. I.; Warren, S. *J. Chem. Soc., Chem. Commun.* **1978**, 657. (c) Babler, J. H.; Invergo, B. J. *J. Org. Chem.* **1979**, *44*, 3723. (d) Masaki, Y.; Sakuma, K.; Hashimoto, K.; Kaji, K. *Chem. Lett.* **1981**, 1283. (e) Hutchins, C. W.; Cooper, G. K.; Pürro, S.; Rapoport, H. *J. Med. Chem.* **1981**, *24*, 773.

(9) Kwart, H.; Benko, D. A. *J. Am. Chem. Soc.* **1979**, *101*, 1277.

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(11) (a) Sharpless, K. B.; Lauer, R. F. *J. Am. Chem. Soc.* **1972**, *94*, 7154. (b) Reich, H. J. *J. Org. Chem.* **1975**, *40*, 2570. (c) Salmond, W. G.; Barta, M. A.; Cain, A. M.; Sobala, M. C. *Tetrahedron Lett.* **1977**, 1683. (d) Clive, D. L. J.; Chittattu, G.; Curtis, N.; Menchen, S. M. *J. Chem. Soc., Chem. Commun.* **1978**, 770. (e) Pennanen, S. I. *Synth. Commun.* **1980**, *10*, 373. (f) Wollenberg, R. H. *Tetrahedron Lett.* **1980**, *21*, 3139. (g) Kametani, T.; Nemoto, H.; Fukumoto, K. *Heterocycles* **1977**, *6*, 1365; *Bioorg. Chem.* **1978**, *7*, 215.

(12) Propargyl and allenyl selenoxides behave similarly: (a) Reich, H. J.; Shah, S. K. *J. Am. Chem. Soc.* **1977**, *99*, 263. (b) Reich, H. J.; Shah, S. K.; Gold, P. M.; Olson, R. E. *Ibid.* **1981**, *103*, 3112. (c) Reich, H. J.; Kelly, M. J. *Ibid.* **1982**, *104*, 1119.

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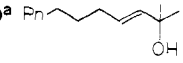
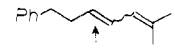
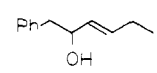
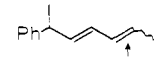
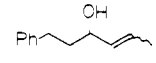
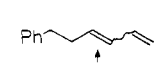
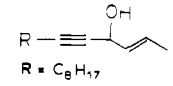
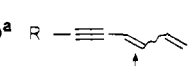
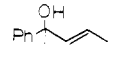
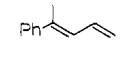
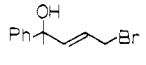
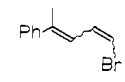
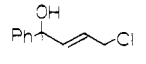
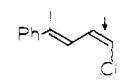
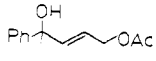
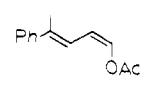
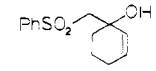
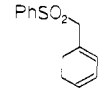
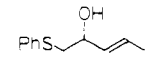
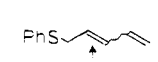
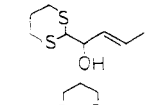
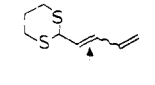
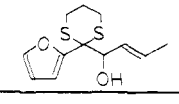
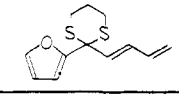
Table I. Diene Formation from Allyl Alcohols According to Scheme I (Ar-Y-X = 2,4-Dinitrobenzenesulfenyl Chloride, 3)

NO	ALLYL ALCOHOL	NO.	DIENE	YIELD	E/Z
1a[a]	 Ar = 2-$CH_3C_6H_4$	2a		83	
1b[a]	2,5-$Cl_2C_6H_3$	2b		66[b]	
1c	C_6H_5	2c		79	
4		22[a]		75	
5a[a]	 Ar = C_6H_5	23a		71	
5b[a]	2,5-$Cl_2C_6H_3$	23b		10	
6		24		88	
7		23a		77	
8		25[a]		68	
9		26		74	
10[a]		27[a]		73	87/13
11[a]		28		54	60/40
12[a]		29		100	85/15
13[a]	 R = C_6H_{17}	30[a]		72	65/35
14		31		85	
15[a]		32		39	c
16[a]		33		17	33/67
17[a]		34		55	
18		35[a]		51	
19		36		69	87/13
20		37[a]		61	>95/5
21		38		62	

[a] Complete experimental procedure given in Experimental Section. [b] See ref 21. [c] See Experimental Section.

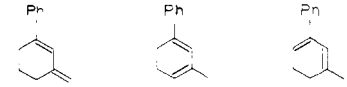
2,4-dinitrobenzenesulfenyl chloride (**3**), we subjected a variety of alcohols to our optimized conditions (1.05–1.10 equiv of **3**,[17] 2.3 equiv of Et_3N) with the results shown in Table I. The benzylic alcohols were converted readily to dienes at room temperature, while most of the other alcohols required higher temperatures. Thus two reaction methods were used. For the more reactive alcohols, ArSCl was added to a methylene chloride solution of alcohol and amine at 0–5 °C and the mixture stirred for several hours at room temperature (method A). Alternatively, ArSCl was added to an ethylene dichloride solution of the alcohol and amine and then refluxed for 1–3 h (method B).

In all cases the sulfenate esters are readily formed at or below room temperature within seconds (the reactions are exothermic) and can be isolated in systems where rearrangement is slow.

The products are easily separated from the majority of ArSX species by diluting the reaction mixture with pentane, followed by filtration, which removes most of the insoluble sulfur-containing materials (ArSCl, ArSOH, etc.). The hydrocarbon products could be easily purified by elution through a short silica gel column with pentane, while the heteroatom-functionalized dienes sometimes required more careful procedures.

Most dehydrations occurred cleanly to give the regiospecific diene as the only product in good yield, even when other isomers were more stable (e.g., **25**, **28**, **36**). The procedure was used to prepare the three isomeric phenyl-1,3-cyclohexadienes (**2c**, **23a**, **25**).

A few systems were problematic. An initial attempt at dehydration of **4** at room temperature (method A) gave a low yield of a mixture of dienes plus 3-methylbiphenyl. At −30 °C, the reaction gives a 75% yield of dienes **22a**, **22b**, and **22c** in a ratio

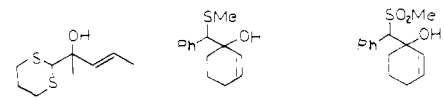


22a 22b 22c

of 66:28:6. Overnight at room temperature, the product mixture isomerizes to give a 1:1:1 ratio. The small amount of 1,2-dehydration product (**22c**) in the initial product is felt to be due to isomerization.

The sulfenate ester of geraniol was unreactive under typical conditions. That is, after 5 h at 53 °C, no myrcene was detected, but cis–trans isomerization of the $C_{2,3}$ bond had occurred, as well as the formation of some material tentatively identified as limonene (a known product of cyclization of the neryl cation) and some unidentified substances; no geraniol was regenerated.

A few sulfur-functionalized allyl alcohols were tested. It was found that secondary allyl alcohols such as **19**–**21** were successfully converted to dienes under typical reaction conditions. Similar tertiary alcohols, i.e., **39** and **40**, did not give useful amounts of



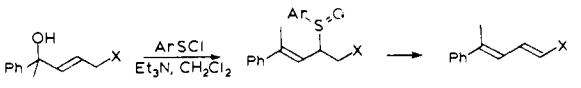
39 40 41

diene under various conditions (triethylamine, pyridine, or sodium hydride as base). The sulfenyl chloride may be attacking the sulfur[18] or the double bond. The sulfone **41** also failed to give a diene. Here, the base sensitivity of the product may be the limiting factor. Sulfone **18** does give diene **35**, but only if pyridine is used as base. Presumably the allylic proton α to sulfonyl is less acidic in **35** than in the diene that would be formed from **41**.

We also investigated systems in which there were other functional groups on the diene itself, i.e., **15**–**17**. In these three molecules, the intermediate sulfoxide must eliminate toward "X".

(17) Some of the conversions were carried out with the unpurified commercial material. Approximately 2.5 equiv were needed for complete conversion of allyl alcohol to diene.

(18) The de-*tert*-butylation of (*S*)-*tert*-butyl-protected cysteine has been reported using *o*-nitrobenzenesulfenyl chloride. Pastuszak, J. J.; Chimiak, A. *J. Org. Chem.* **1981**, *46*, 1868.



15 X = Br
16 X = Cl
17 X = OAc

On the basis of previous results in our laboratory and others[19] which demonstrated that elimination of selenoxides toward oxygen functionality was extremely slow, we anticipated the acetate **17** to pose problems. In fact, the dienol acetate was formed readily at room temperature, through it decomposed easily during purification.

The bromide **15** and the chloride **16** both gave low yields of dienes. On the assumption that triethylamine was forming a quaternary ammonium salt with the halides faster than elimination was occurring, diisopropylethylamine was used as base. It did not seem to improve the yield of diene from **16** (17%). However, pyridine gave an improved yield (39%) of **32** from **15**.

Geometry of the Dienes. In all acyclic compounds the dienes were carefully examined for isomeric mixtures by ^{1}H NMR. Both the [2,3] sigmatropic rearrangement and the elimination generate predominantly *E* double bonds, though mixtures were found in almost all cases. The geometry of the double bond generated upon [2,3] rearrangement represents the thermodynamic mixture of sulfoxides; that is, several rearrangements may occur before the sulfoxide fragments. This was demonstrated by the dehydration of two different isomeric mixtures of the same alcohol, **12** (*E*:*Z* = 74:26 and 15:85), giving the same *E*:*Z* ratio of product dienes **29** (85:15).

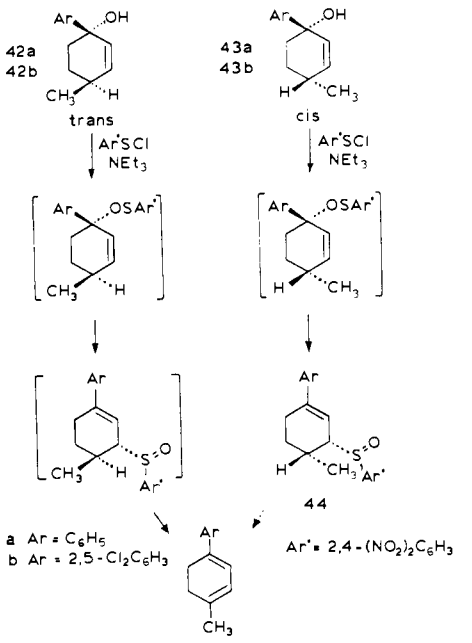
Stereochemistry. When this investigation was initiated, the unexpectedly rapid formation of dienes cast some doubt upon the mechanism of reaction. To help distinguish between the mechanism proposed here and alternate routes in which direct 1,4 elimination or rearrangement to some species that undergoes a 1,2-base elimination occurs, we carried out a study of the reaction stereochemistry using the *cis*- and *trans*-methylcyclohexenols **42** and **43** (Scheme II). According to the proposed mechanism, the trans alcohol **42** should give diene, while the cis alcohol **43** should not.

The alcohols were easily prepared by ArLi addition to 4-methyl-2-cyclohexenone and separation by TLC or HPLC. Stereochemistry of **42a** and **43a** (Ar = Ph) was assigned by hydrogenation to the known saturated alcohols and comparison to the reported NMR spectra.[20] The 2,5-dichlorophenyl alcohols **42b** and **43b** were identified by comparison to the phenyl system. Particularly characteristic are the coupling constants between the β-olefinic proton and the allylic proton adjacent to it. In the trans alcohol, the dihedral angle between the protons is small (~10–15°) and the coupling constant is larger (**42a**, 2.9 Hz; **42b**, 3.3 Hz) than that in the cis isomer (**43a**, <1 Hz; **43b**, 1.8 Hz), where the dihedral angle is almost 90°. Furthermore, **42b** and **43b** exhibited similar TLC retention times to **42a** and **43a**, respectively. In both systems, the trans alcohols were formed as the major product (axial attack of ArLi on enone).

The phenyl system (**42a** and **43a**) was examined first. Under typical reaction conditions, the trans alcohol **42a** formed the diene almost instantaneously at room temperature as expected. The cis alcohol decomposed to give the diene also, though complete diene formation took several hours. The possibility of base elimination in the latter case was ruled out upon the observance of similar decomposition rates of the sulfenate ester in the presence of several very different amine bases (Et_3N, 2,5-di-*tert*-butylpyridine, 1,8-bis(dimethylamino)naphthalene).

The 2,5-dichlorophenyl system was studied in the hopes that nonstereospecific carbonium ion pathways for decomposition would be less favored since the ortho chloro group should cause the ring

Scheme II



to twist so that stabilization of the allyl carbonium ion is decreased.[21]

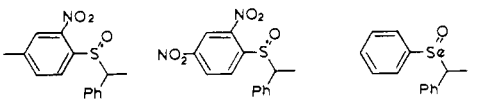
The trans alcohol **42b** cleanly gave the diene at room temperature within 60 min. When the cis alcohol **43b** was treated with $ArSCl–Et_3N–CH_2Cl_2$, no diene was formed. Instead, a new compound was isolated exhibiting the spectral properties expected of the sulfoxide **44b** (diene appears after several days at 25 °C).

The NMR of **44b** exhibited several features: (1) an allylic transposition had occurred, as evidence by a disappearance in the olefinic protons at δ 5.66 and 5.85 and the appearance of new protons at δ 4.88 and 3.90 (the chemical shifts of the 2,5-dichlorophenyl group are similar to those in **5b** and **2b** and unlike those in **1b**) and (2) the protons of the 2,4-dinitrophenyl group have chemical shifts consistent with attachment to an electron-withdrawing sulfoxide moiety rather than a sulfide or sulfenate.

IR spectral data was inconclusive; the S–O stretch at ~1000–1100 cm^{-1} was particularly weak (as compared with other vibrational modes of the molecule). The material could not be purified sufficiently for an elemental analysis.

These results, together with those of Rapoport and co-workers[8e] on the successful 1,4 dehydration of isocodeine (whereas codeine, which lacks a syn hydrogen, gives only the allylic sulfoxide), substantiate the proposed overall syn stereochemistry of the reaction. However, the eventual formation of a diene from **42a** and **42b** demonstrates that other elimination mechanisms become competitive when syn elimination is prohibited.

Rate of Reaction. Alkyl phenyl sulfoxides are stable to elimination at room temperature. The success of the reagent in our case is due to two factors previously demonstrated to increase elimination rates: the electron-withdrawing substituents on the aromatic ring[22] and the allylic nature of the sulfoxide (in analogy with benzylic selenoxides[19a]). These effects are illustrated for two benzylic sulfoxides (**45** and **46**) that show first-order elimination



45 46 47

$t_{\frac{1}{2}}$ (38°C) = 14 h 1.5 h < 1 min

rates of $k = 1.39 \times 10^{-5}$ s^{-1} for **45** and $k = 1.3 \times 10^{-4}$ s^{-1} for **46** at 38 °C. For comparison, 1-phenylethyl phenyl selenoxide (**47**) has $k \gtrsim 1.5 \times 10^{-2}$ s^{-1}.

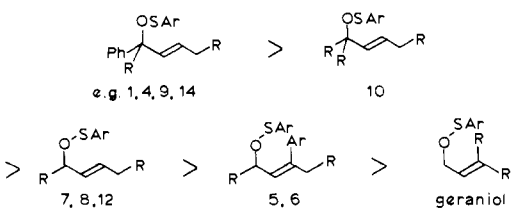
(19) (a) Reich, H. J.; Wollowitz, S.; Trend, J. E.; Chow, F.; Wendelborn, D. F. *J. Org. Chem.* **1978**, *43*, 1697. (b) Sharpless, K. B.; Lauer, R. F. *Ibid.* **1974**, *39*, 429. (c) Hori, T.; Sharpless, K. B. *Ibid.* **1978**, *43*, 1689.

(20) Geneste, P.; Herrman, P.; Kamenka, J. M.; Pons, A. *Bull. Soc. Chim. Fr.* **1975**, 1619.

(21) Reich, I. L.; Reich, H. J. *J. Org. Chem.* **1981**, *46*, 3721.

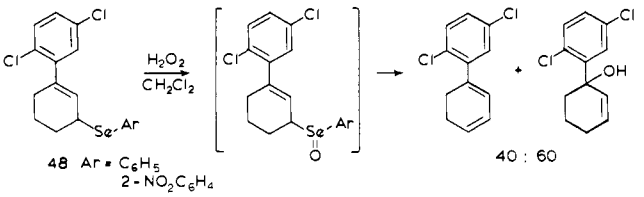
(22) Emerson, D. W.; Korniski, T. J. *J. Org. Chem.* **1969**, *34*, 4115.

The dependence of the overall reaction rate on the structure of the allylic alcohol is illustrated by the following order of relative rates:



The reaction conditions needed for the formation of the diene ranged from a few minutes at or below room temperature for the most reactive compounds to hours at 50 to 80 °C for the least reactive, with the additional penalty of poor yields. The situation can be summarized in terms of the substitution of the double bond before and after [2,3] sigmatropic rearrangement, i.e., in terms of the position of the sulfenate–sulfoxide equilibrium of Scheme I. Thus, allyl alcohols in which the double bond is more highly substituted or conjugated in the sulfoxide than the sulfenate will tend to form dienes rapidly, whereas those where the double bond migrates to a less substituted position during formation of sulfoxide tend to be sluggish[23] or plagued with side reactions. Compound **5b** gave only a poor yield of the diene, whereas geraniol gave none under the reaction conditions we tried.

Formation and Reactivity of Selenenate Esters. As was mentioned earlier, *o*-nitroareneselenenate esters could be formed easily by the same procedure as that used for the sulfur system. However, subsequent steps were not as successful as with sulfur. Dehydration of alcohol **1a** with 4-methyl-2-nitrobenzeneselenenyl chloride yielded diene **2a** in 65% yield only after 12 h at 38 °C (2,4-dinitrobenzenesulfenyl chloride required several minutes at 25 °C). The selenenate ester formed upon reaction of **1a** with 2,4-dinitrobenzeneselenenyl bromide did not rearrange and give diene but slowly hydrolyzed back to alcohol over 16 h at 25 °C. Diene formation in the former case represents the first demonstration of reversibility of the allyl selenoxide rearrangement.[24] That the difficultly with selenium lies in the rearrangement step and not in the syn elimination was substantiated by the following experiment: oxidation of selenide **48** gave, at 25 °C, the diene plus rearranged alcohol in minutes.[21]



Our initial results with selenium suggest several characteristics of the selenoxide–selenenate equilibrium. The rate of conversion of selenenate to selenoxide is decreased with increasing electron-withdrawing substituents on the aryl ring, as has been shown for sulfur and analogues.[5] The slowness of this reaction coupled with the rapidity of the reverse reaction indicates that selenenate is much more strongly favored in the equilibrium of the selenoxide–selenenate than is sulfenate in the sulfoxide–sulfenate equilibrium. We have recently presented our initial results of a quantitative study of a similar equilibrium that is in accord with these observations.[25]

Conclusions

The simple procedure developed here has been shown to cleanly give a net 1,4 dehydration of many allyl alcohols at moderate temperatures and under mildly basic conditions. The overall stereochemistry is cis, and the reaction promises to be quite tolerant of functional groups. Limitations on the reaction are of two types: (1) if the [2,3] sigmatropic equilibrium favors sulfenate too strongly, the reaction will be sluggish and may give poor yields; (2) if the allyl carbonium ion formed by ionization of allyl sulfenate is exceptionally stabilized, yields or regioselectivity may be poor.

Applicability of selenenyl halides to the 1,4 dehydration of allyl alcohols is severely limited since the [2,3] sigmatropic selenoxide–selenenate equilibrium is too strongly shifted toward the latter.[25]

Table II. Reaction Conditions for Diene Formation (Structures Are Shown in Table I)

no.	mmol	ArSCl,[a] mmol	Et_3N, mmol	method[b]	reaction time, h	product no.	yield, g (%)
1a	1.01	1.09	2.1	A	2	2a[c]	0.119 (71)
	0.136	0.112[d]	0.24	*e*	12.5		0.014 (65)
1b	10.0	25.0	50.0	A	0.8	2b[c]	1.77 (83)[f]
	0.83	1.8[d]	2.0	*e*	20		0.10 (54)
1c	1.78	4.1[g]	4.4	A	2	2c[c]	0.219 (79)
4	1.58	3.7[g]	3.9	C		22[c]	0.200 (75)
5a	1.65	3.8[g]	4.1	B	2.5	23a[c]	0.183 (71)
5b	1.49	1.6	3.4	B	2	23b	(<10)
6	1.61	3.7[g]	3.9	B	5	24	0.262 (88)
7	1.86	4.2[g]	4.6	B	3	23a[c]	0.223 (77)
8	1.64	4.7[g]	5.1	B	2.5	25[c]	0.175 (68)
9	0.89	2.2[g]	2.2	A	2.5	26	0.102 (74)
10	12.8	30[g]	32.0	A	16	27[c]	1.800 (77)
11	1.02	2.4	2.6	B	1.5	28[c]	0.095 (54)
12	2.02	2.08	4.5	B	0.8	29[c]	0.319 (100)
13	5.82	6.1	12.2	A	0.5	30	0.896 (72)
14	1.73	1.8	3.6	A	0.3	31[c]	0.214 (85)
15	1.46	1.5	3.1[h]	A	1.5	32[c]	0.127 (39)
16	1.00	1.1	2.2[i]	A	0.8	33	0.030 (17)
17	1.57	1.7	3.3	A	1.5	34[c]	0.174 (55)
18	12.3	14.6	35.0[h]	A	2	35	1.47 (51)
19	1.98	2.6	5.9	B	0.8	36[c]	0.245 (69)
20	2.08	2.5	5.0	B	0.8	37	0.220 (61)
21	1.09	1.3	2.7	B	0.6	38	0.160 (62)

[a] 2,4-Dinitrobenzenesulfenyl chloride. [b] (Method A) ArSCl added to a chilled solution of alcohol and base in CH_2Cl_2 (0.1–0.5 M). After 5 min, solution let stir at room temp the specified time. (B) ArSCl added to a similar solution of ethylene dichloride. After 5 min, quickly heated to reflux for the reaction time. (C) Reacted at −40 °C, let warm to 0 °C during 4 h. [c] Isolation: At room temp, dilution with 2–3 volumes pentane, filtered and concentrated. Purification completed by elution through silica gel with pentane. [d] 4-Methyl-2-nitrobenzeneselenenyl chloride. [e] Reflux in CH_2Cl_2. [f] See ref 21. [g] Unrecrystallized ArSCl used. See ref 17. [h] Pyridine used as base. [i] Ethyldiisopropylamine used as base.

Experimental Section

General Procedures. Nuclear magnetic resonance spectra were obtained on a JEOL MH-100 in CCl_4 with tetramethylsilane as an internal standard unless otherwise specified; 270-MHz spectra were recorded on a Brucker WH-270 WHz spectrometer. Infrared spectra were taken on a Beckman IR-8 or a Perkin-Elmer IR-267, mass spectra on an AE1MS-902 spectrometer. Preparative thin-layer chromatography was carried out with Merck PF-254 or NM-Kieselgel P/UV_{254} silica gel. Elemental analyses were performed by Spang Microanalytical Labs. or by Galbraith Labs, Inc. Melting points were uncorrected.

THF and reagent ether were freshly distilled from sodium benzophenone ketyl. All reactions were carried out under nitrogen atmosphere. The 2,4-dinitrobenzenesulfenyl chloride (**3**) was purchased from Aldrich Chemical Co. and recrystallized from CCl_4.[17]

Literature procedures were used to prepare 1-(2,5-dichlorophenyl)-2-cyclohexen-1-ol (**1b**),[21] 2-phenyl-2-cyclohexen-1-ol (**7**),[26] and 4-methyl-2-nitrophenyl selenocyanate.[27]

(23) 2-Cyclohexenyl 2,4-dinitrobenzenesulfenate is reported to be quite stable: Zefirov, N. S.; Abdulvaleeva, F. A. *Zh. Org. Khim.* **1971**, *7*, 947.

(24) Some results recently reported by Halazy, S.; Krief, A. (*Tetrahedron Lett.* **1981**, *22*, 2135) can also provide evidence for reversibility of the rearrangement.

(25) Reich, H. J.; Wollowitz, S. In "Selenium in Biology and Medicine", Spallholz, J. E., Martin, J. L., Ganther, H. E., Eds.; Avi: Westport, CT, 1981; p 460.

(26) Treibs, W.; Weissenfels, M. *Chem. Ber.* **1960**, *93*, 1374.

(27) (a) Bauer, H. *Chem. Ber.* **1913**, *46*, 92. (b) Sharpless, K. B.; Young, M. W. *J. Org. Chem.* **1975**, *40*, 947.

Table II gives experimental conditions for diene formation. The yields reported are for compounds to whose purity, as established by NMR spectroscopy, was greater than 93% unless indicated otherwise.

4-Methyl-2-nitrobenzeneselenenyl chloride was prepared from the selenocyanate via the methyl selenide. The selenide was prepared by slow addition of $NaBH_4$ (0.200 g, 5.26 mmol) to a suspension of 4-methyl-2-nitrophenyl selenocyanate[27] (1.23 g, 5.10 mmol) in 20 mL of 95% EtOH under N_2. After 20 min, MeI (0.65 mL, 10.4 mmol) was added and the suspension stirred for 2 h. The selenide was then taken up in ether and washed with 1.2 N HCl, aqueous $NaHCO_3$, and saturated aqueous NaCl, dried, and concentrated to give 1.01 g (86%) of 4-methyl-2-nitrophenyl methyl selenide; mp 63.5–64.5 °C (lit. mp 66.5–67.5 °C).[28]

To 0.83 g (3.61 mmol) of the selenide in 5 mL of ethylene dichloride was added thionyl chloride (0.30 mL, 4.1 mmol). After stirring for 15 min, the resulting suspension was refluxed for 2 h, then cooled to room temperature, and concentrated. Crystallization from ether–pentane gave 0.51 g (56%) of bright orange needles: mp 79.0–80.0 °C; IR ($CDCl_3$) 1515, 1470 (m), 1323 (m), 1280 (m), 1110 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.40 (s, 3 H), 7.45 (br d, J = 8 Hz, 1 H), 7.84 (d, J = 8 Hz, 1 H), 7.96 (br s, 1 H).

1-(*o*-Tolyl)-2-cyclohexen-1-ol (1a). 2-Iodotoluene (2.55 mL, 20.0 mmol) in 8 mL of ether was cooled to 0 °C under N_2. *n*-BuLi (1.49 M, 13.52 mL, 20.1 mmol) was added slowly. After 5 min, the solution was cooled to −78 °C, and 2-cyclohexenone (1.86 mL, 19.1 mmol) in 10 mL of ether was added slowly. The solution was allowed to warm to 0 °C over 20 min, and the reaction was quenched with ice–water. The ether layer was washed with aqueous NaCl solution, dried, and concentrated. The product crystallized to 3.12 g (87%) of thick needle crystals; mp 76–77 °C; ^1H NMR (CCl_4) δ 1.5–2.4 (m, 7 H), 2.48 (s, 3 H), 5.80 (d, J = 10, 1 H), 5.98 (dt, J = 10, 3 Hz, 1 H), 7.1 (m, 3 H), 7.55 (m, 1 H); MS 188.1201 (M^+), calcd for $C_{13}H_{16}O$, 188.1201.

3-Phenyl-2-cyclohexen-1-ol (5a). Alcohol **1a** (0.398 g, 2.29 mmol) and *p*-toluenesulfonic acid (0.021 g, 0.11 mmol) were stirred in 5 mL of a 4:1 dioxane–H_2O solution for 30 min (longer times lead to dehydration). Workup and purification by column chromatography with pentane and then ether gave 0.385 g (97%) of the rearranged alcohol **5a**, which was crystallized from ether–pentane: mp 59–60 °C (lit. mp 59–60 °C,[29a] 60–61 °C);[29b] ^1H NMR δ 1.5–2.1 (m, 5 H), 2.38 (m, 2 H), 4.30 (m, 1 H), 6.10 (m, 1 H), 7.2–7.4 (m, 5 H).

3-(2,5-Dichlorophenyl)-2-cyclohexen-1-ol (5b) was prepared similarly to **5a** but required refluxing for 75 min. The alcohol (1.09 g, 100%) was obtained as a very viscous oil: IR (neat) 3300 (br), 1650 (w), 1580 (m), 1550 (m), 1455, 1095, 1070, 1040, 985, 810 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.5–2.0 (m), 2.2 (m) total 7 H, 4.30 (m, 1 H), 5.66 (dt, J = 3, 1.5 Hz, 1 H), 7.1 (m, 3 H); MS (M^+) 242.0265, calcd for $C_{12}H_{12}Cl_2O$, 242.0265.

2-Methyl-7-phenyl-3-hepten-2-ol (10).[11b] Prenyl phenyl selenide (0.458 mL, 2.5 mmol) in 4.5 mL of THF was cooled to 0 °C under N_2. Lithium diisiopropylamine (LDA) (1.2 M, 2.10 mL, 2.5 mmol) was added dropwise, and the solution was stirred for 30 min. 1-Bromo-3-phenylpropane (0.375 mL, 2.56 mmol) was added, and the solution was allowed to stir for 75 min. Upon workup, 0.90 g of oil was obtained, which was dissolved in 6 mL of CH_2Cl_2 containing 0.4 mL (5 mmol) of pyridine, and 30% H_2O_2 (0.80 mL, 8 mmol) in 1 mL of water was added very slowly. After 10 min, the mixture was worked up to give the crude alcohol: TLC (1:19:80 NEt_3–ether–pentane, R_f 0.35) gave 0.435 g (85%) of pure alcohol; IR (neat) 3400 (br), 2980, 2935, 1500, 1460, 1380, 1378, 1150, 980, 750, 700 cm^{-1}; ^1H NMR δ 1.20 (s, 6 H), 1.65 (m, 2 H), 2.0 (m, 2 H), 2.55 (t, J = 7–8 Hz, 2 H), 3.0 (br s, 1 H), 5.55 (br s, 2 H), 7.10 (m, 5 H); MS 204.15155 (M^+), calcd for $C_{14}H_{20}O$, 204.15141.

2-Phenyl-4-hepten-3-ol (11).[16] A solution of *m*-CPBA (85%, 0.792 g, 3.91 mmol) in 3.5 mL of THF was added to butyl phenyl selenide (0.683 mL, 3.90 mmol) in 1.5 mL of THF at 0 °C. After 30 min, the solution was cooled to −78 °C, LDA (1.0 M, 9.35 mL, 9.35 mmol) was added, and then after 20 min, 2-phenylpropionaldehyde (0.522 g, 3.90 mmol) in 25 mL of THF was added. After 20 min, the cold bath was removed, glacial HOAc (0.33 mL) in 1 mL of THF was added, and the mixture was quickly poured into 50 mL of refluxing CCl_4 for 35 min. After workup, treatment with 30% H_2O_2 (1 mL + 1 mL of H_2O) in CH_2Cl_2 for 20 min and then workup again, TLC (20% ether–pentane, R_f ~ 0.4–0.5) gave 0.311 g (42%) of the allyl alcohol as a mixture of diastereomers; IR (neat) 3210 (br), 2980, 1500, 1460, 1020, 980, 770, 710 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.9 (t, J = 7 Hz, 3 H), 1.25 (d, J = 7 Hz, 3 H), 1.95 (br pentuplet, J = 7 Hz, 2 H), 2.35 (br s, exchange with D_2O, 1 H), 2.80 (pentuplet, J = 6 Hz, 1 H), 4.07 (t, J = 6 Hz, 1 H), 5.1–5.8 (m, 2 H), 6.9–7.4 (m, 5 H); MS 190.1355 (M^+), calcd for $C_{13}H_{18}O$, 190.1358.

1-Phenyl-4-hexen-3-ol (12). With the use of the general procedure of Normant,[30] propenylmagnesium bromide was prepared and treated with 3-phenylpropionaldehyde. After workup, bulb-to-bulb distillation (60–70 °C, 0.10–0.17 mmHg) gave 2.89 g (77%) of the allyl alcohol as a 74:26 cis–trans mixture as determined by ^1H NMR: δ 1.6–2.0 (m, 5 H), 2.68 (t, J = 8 Hz, 2 H), 4.02 (br q, J = 7 Hz), 4.48 (br q, J = 7 Hz) total 1 H, 74:26 ratio, 5.16–5.8 (m, 2 H), 7.2 (m, 5 H). Spectrum at 270 MHz ($CDCl_3$) shows the cis compound 1.63 (d, J = 6.8 Hz) and 5.4 (dd, J = 11, 8–9 Hz). The trans compound showed protons at 1.69 (d, J = 6.2 Hz), 5.51 (dqd, J = 15.3, 6.3, 0.7 Hz), and 5.66 (ddq, J = 15.26, 6.8, 1.3 Hz).

Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.69; H, 9.07.

The alcohol **12** was also prepared similarly to **11** from propyl phenyl selenide and hydrocinnamaldehyde to give the alcohols in a 15:85 cis–trans ratio; IR (neat) 3380 (br, s), 1680 (w), 1615 (w), 1505, 1463, 1065, 980, 760, 710 cm^{-1}.

2-Tetradecen-5-yn-4-ol (13). MeLi (1.38 M, 8 mmol) was added slowly to 1-decyne (1.08 g, 7.8 mmol) in THF at 0 °C. After 20 min, the solution was cooled to −78 °C and crotonaldehyde (0.655 mL, 7.9 mmol) in THF was dripped in. After an additional 20 min at that temperature, the reaction was quenched, and the solution worked up, concentrated, and distilled (Kugelrohr, 0.35 mm, bath 75–80 °C) to give 1.35 g of **13** (83% yield): ^1H NMR δ 0.85 (m, 3 H), 1.25 (m, ~12 H), 1.68 (d, J = 5–6 Hz, 3 H), 2.10 (m, 2 H), 3.25 (br s, 1 H), 4.65 (br d, J = ~4–5 Hz, 1 H), 5.55 (dd, J = 16, 5 Hz), 5.76 (dq, J = 16, 6 Hz); MS (M^+) 208.1822, calcd for $C_{14}H_{24}O$, 208.1827.

5-Bromo-2-phenyl-3-penten-2-ol (15). 2-Phenyl-3-penten-2-ol (0.902 g, 80% pure, 4.45 mmol) and freshly recrystallized *N*-bromosuccinimide (0.990 g, 5.56 mmol) were refluxed in 8 mL of CCl_4 under a sunlamp for 45 min. Filtration and TLC (1:9:90 Et_3N–ether–pentane, R_f 0.15) gave 0.665 g (62%) of the brominated allyl alcohol: IR (neat) 3550 (br), 3400 (br), 2970, 1600 (w), 1490, 1445, 1205, 970, 765, 700 cm^{-1}; ^1H NMR δ 1.45 (s, 3 H), 3.5 (br s, 1 H), 3.75 (d, J = 6 Hz, 2 H), 5.85 (m, 2 H), 7.1–7.4 (m, 5 H); MS (30 eV), *m/e* (rel. intensity) 161 (3.3), 143 (32.7), 129 (18.4), 128 (28.6), 121 (4.7), 105 (26.8), 82 (11.3), 77 (15.3), 43 (100).

The major impurity, tentatively assigned as 4-bromo-3-phenyl-2-pentanone, had the following ^1H NMR: δ 1.97 (d, J = 7 Hz, 3 H), 2.07 (s, 3 H), 3.98 (d, J = 10–11 Hz, 1 H), 4.70 (dq, J = 10, 7 Hz, 1 H), 7.2 (m, 5 H).

5-Chloro-2-phenyl-3-penten-2-ol (16). Bromide **15** (0.251 g, 1.05 mmol) and benzyltriethylammonium chloride (0.995 g, 4.37 mmol) were stirred in 6 mL of CH_3CN for 15 h. Concentration and trituration of the solid residue with 4 × 3 mL of ether gave 0.203 g of the chloride, ≳99% pure by NMR: IR (neat) 3550 (br), 3400 (br), 2970, 1610 (w), 1501 (m), 1455, 1260 (m), 983, 775, 712, 692 (m) cm^{-1}; ^1H NMR δ 1.40 (s, 3 H), 2.70 (br s, 1 H), 3.73 (d, J = 6 Hz, 2 H), 5.66 (dt, J 16, 6 Hz), 5.82 (d, J = 16 Hz) AB total 2 H, 7.0–7.3 (m, 5 H); MS 196.0670 (M^+), calcd for $C_{11}H_{13}ClO$, 196.0655.

5-Acetoxy-2-phenyl-3-penten-2-ol (17).[11b] A solution of allyl phenyl selenide (2.50 mL, 12.7 mmol) in 10 mL of THF was cooled to −78 °C under N_2 in a flask with an efficient stirrer. LDA (12.8 mL, 1.0 M, 12.8 mmol) was added over 3 min and the resulting slurry stirred for 20 min. A suspension of $ZnCl_2$ (untreated, 0.888 g, 6.53 mmol) in 7 mL of ether was added, and then after 25 min, acetophenone (1.35 mL, 11.5 mmol) in 5 mL of THF was added and stirring continued 25 min more. After workup and concentration, starting material was removed by bulb-to-bulb distillation, leaving the crude product as a 1:1 mixture of α- and γ-alkylated material.

The mixture was oxidized as in the preparation of **10** and worked up. Crystallization from ether–pentane gave 0.359 g (48%) of 4-phenyl-2-pentene-1,4-diol: mp 112–113 °C; IR (KBr) 3300–3200 (br), 1495, 1448, 1328, 1200, 1183, 1032, 1005, 970, 912, 870, 770, 695 cm^{-1}; ^1H NMR (acetone-d_6) δ 1.53 (s, 3 H), 3.1 (br s, >2 H), 4.06 (d, J = 4–5 Hz, 2 H), 5.84 (dd, J = 17 Hz, 4 Hz), 5.98 (d, J = 17 Hz) total 2 H, AB pattern of an ABX_2, 7.2–7.6 (m, 5 H).

Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.19; H, 7.97.

The diol (0.331 g, 1.86 mmol) was converted to **17** upon brief (10 min) heating with 1.0 mL of acetic anhydride and 1.5 mL of pyridine, followed by workup giving 0.396 g (89%, 91% pure, pyridine present); ^1H NMR δ 1.53 (s, 3 H), 1.89 (s, 3 H), 3.82 (br s, 1 H), 4.45 (d, J = 4–5 Hz, 2 H), 5.72 (dt, J = 16 Hz, 5–6 Hz), 5.97 (d, J = 16 Hz) total 2 H, AB part of an ABX_2 pattern, 7.1–7.45 (m, 5 H).

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Dehydration Procedures. The reaction conditions for dehydration of the alcohols using 2,4-dinitrobenzenesulfenyl chloride are shown in Table II. (CAUTION—the formation of the sulfenate esters is exothermic; ArSCl should be added slowly for large-scale reactions.) The dienes are treated in order of compound number. For typical complete experimental procedures, see compounds **27**, **30** (method A using NEt_3), **35** (method A using pyridine), **25**, **37** (method B), and **22** (method C). Preparation of compound **2b** is described by use of 2-nitro-4-methylbenzeneselenenyl chloride.

1-(2-Methylphenyl)-1,3-cyclohexadiene (2a, Method A): ^1H NMR δ 2.20 (br s, 7 H), 5.8 (m, 2 H), 6.0 (m of dd, J = 9, 6 Hz, 1 H), 7.03 (s, 4 H); MS 170.1085 (M^+), calcd for $C_{13}H_{14}$, 170.1095.

1-(2,5-Dichlorophenyl)-1,3-cyclohexadiene (2b) Using Areneselenenyl Chloride. To a solution of 0.201 g (0.83 mmol) of 1-(2,5-dichlorophenyl)-2-cyclohexen-1-ol (**1b**) and 0.28 mL (2 mmol) of NEt_3 in 4 mL of CH_2Cl_2 was added 0.445 g (1.78 mmol) of 2-nitro-4-methylbenzeneselenenyl chloride, and the solution was refluxed under N_2 for 20 h. Pentane (15 mL) was added, the mixture was filtered, and the concentrated filtrate was purified by elution through a short column of silica gel with pentane to give 0.100 g (54%) of **2b**, identical with authentic material.[21]

1-Phenyl-1,3-cyclohexadiene (2c, Method A): mp 40.5–41.0 °C (lit. mp[31] 38–39 °C); ^1H NMR ($CDCl_3$, 270 MHz) δ 2.33 (m, 2 H), 2.60 (app t, J = 10.5 Hz, 2 H), 5.89 (dt, J = 9.2, 4.5 Hz, 1 H), 6.09 (m, 1 H), 6.32 (br d, J = 5.1 Hz, 1 H), 7.2 (m), 7.3 (m), 7.4 (m) total 5 H; ^{13}C NMR ($CDCl_3$) δ 23.1, 25.2, 120.7, 124.8, 125.1, 125.7, 126.8, 128.2, 136.2, 141.1.

Dehydration of Alcohol 4 To Give Olefins 22a–c. 1-Phenyl-3-methyl-2-cyclohexen-1-ol (**4**) (0.297 g, 1.58 mmol) and Et_3N (0.553 mL, 3.95 mmol) were cooled to −35 °C in 10 mL of dry CH_2Cl_2. 2,4-Dinitrobenzenesulfenyl chloride (0.870 g, unrecrystallized) was added slowly, and the suspension was stirred 0.5 h and then warmed to 0 °C over 3.5 h. Pentane (30 mL) was added, the mixture was filtered, and the filtrates were concentrated. Elution through a silica gel plug with pentane gave 0.200 g (75%) of the dienes **22a**, **22b**, and **22c** in a 66:28:6 ratio. The mixture showed multiplets of δ 1.8, 2.1–2.3, and 7.0–7.4. On the basis of our assignments: the olefinic peaks of **22a** were broadened singlets at δ 4.82, 4.90, and 6.55; **22b** showed a multiplet at δ 5.50 and a broad singlet at 6.15; **22c** showed multiplets at δ 5.85 and 6.05.

Anal. Calcd for $C_{13}H_{14}$: C, 91.71; H, 8.29. Found: C, 91.77; H, 8.15.

2-Phenyl-1,3-cyclohexadiene (23a, Method B): ^1H NMR δ 2.25 (m, 4 H), 6.05 (m, 2 H), 6.39 (br d, J = 10–11 Hz, 1 H), 7.30 (m, 5 H) is in agreement with the literature spectrum.[32] This diene was especially prone to decomposition as has been noted by previous workers.[31]

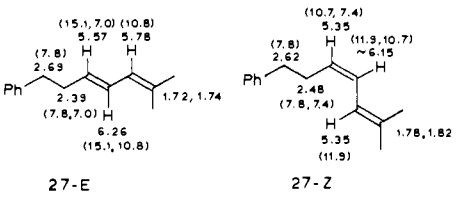
6,6-Dimethyl-2-phenyl-1,3-cyclohexadiene (24, Method B): ^1H NMR δ 1.05 (s, 6 H), 2.15 (dd, J = 4–5, 2–3 Hz, 2 H), 5.72 (br s, 1 H), 5.90 (dt, J = 10, 4–5 Hz, 1 H), 6.30 (d of m, J = 10 Hz, 1 H), 7.3 (m, 5 H).

Anal. Calcd for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 91.06; H, 8.82.

6-Phenyl-1,3-cyclohexadiene (25, Method B). To a solution of 0.266 g (1.64 mmol) of 6-phenyl-2-cyclohexen-1-ol (**8**) and 0.72 mL (5.1 mmol) of NEt_3 in 15 mL of 1,2-dichloroethane was added 1.11 g (4.7 mmol) of 2,4-dinitrobenzenesulfenyl chloride, and the mixture was rapidly heated and refluxed for 2.5 h. The reaction mixture was poured into 50 mL of pentane, filtered, and solvent removed from the filtrate. Elution through a plug of silica gel with pentane gave 0.175 g (68%) of a colorless oil:[33] ^1H NMR δ 2.1–2.6 (m, 2 H), 3.6 (br t, J = 12 Hz, 1 H), 5.6–6.2 (m, 4 H), 7.35 (br s, 5 H); ^{13}C NMR δ 31.63, 39.86, 123.83, 125.32, 126.15, 127.20, 127.42, 128.24, 129.90, 145.30.

1-Phenyl-1,3-cycloheptadiene (26, Method A). After reaction was complete, 10 mL of pentane was added, the suspension was filtered, and the residue was rinsed with 10 mL of 50% ether–pentane. The filtrates were rinsed with 1.2 N HCl and aqueous NaCl and concentrated: TLC (10:90, ether–pentane, R_f 0.8) gave 74% of the diene; ^1H NMR δ 2.00 (pentuplet, $J \sim 5$ Hz, 2 H), 2.35 (m, 2 H), 2.70 (dd, J = 5–6, 3–4 Hz, 2 H), 5.7–6.1 (m, 3 H), 7.2 (m, 5 H); MS 170.1096 (M^+), calcd for $C_{13}H_{14}$, 170.1096.

2-Methyl-7-phenyl-2,4-heptadiene (27, Method A). Alcohol **10** (2.61 g, 12.8 mmol) and triethylamine (4.5 mL, 32 mmol) at 0 °C in 75 mL of dry CH_2Cl_2 were slowly treated with 2,4-dinitrobenzenesulfenyl chloride (unrecrystallized 7.06 g). The suspension was stirred for 16 h at 25 °C. Pentane (100 mL) was added, the slurry was filtered, and the filtrate was rinsed with another 100 mL of pentane. Concentration and elution through 55 g of silica gel with 99:1 pentane–Et_3N gave 1.84 g (77%) of the diene: bp ~ 65 °C (0.3 mmHg); IR (neat) 3020, 2935, 1670 (w), 1615 (m), 1505, 1461, 1390 (m), 968, 752, 702 cm^{-1}; MS 186.1401 (M^+), calcd for $C_{13}H_{12}$, 186.14085; ^1H NMR (270 MHz, $CDCl_3$) showed a 87:13 E:Z mixture. The ^1H NMR data summarized were obtained with the help of decoupling experiments.



27-E 27-Z

6-Phenyl-2,4-heptadiene (28, Method B). Elution of the crude product through silica gel (~5 g) with pentane gave 54% of the diene as a 65:35 mixture of two isomers, which were separated by TLC on 8% $AgNO_3$–silica gel (10:90, ether–pentane). The major isomer (R_f 0.82) was (*E*,*E*)-6-phenyl-2,4-heptadiene: ^1H NMR (C_6D_6, 270 MHz) δ 1.26 (d, J = 7.0 Hz, 3 H), 1.59 (d, J = 6.2 Hz, 3 H), 3.34 (dq, J = 7.0, 6.8 Hz), 5.49 (m, 1 H), 5.7 (m, 1 H), 6.0 (m, 2 H), 7.15 (m, 5 H). The minor isomer (R_f 0.65) was (*Z*,*E*)-6-phenyl-2,4-heptadiene: ^1H NMR (acetone-d_6, 270 MHz) δ 1.36 (d, J = 7.0 Hz, 3 H), 1.71 (dd, J = 7.1, 1.9 Hz, 3 H), 3.56 (pentuplet, J = 7 Hz, 1 H), 5.39 (m, 1 H), 5.83 (dd, J = 15.1, 7.2 Hz, 1 H), 5.99 (m, 1 H), 6.43 (ddt, J = 15.3, 11.0, 1.1 Hz, 1 H), 7.2 (m, 5 H).

Anal. Calcd for $C_{13}H_{16}$: C, 90.64; H, 9.36. Found: C, 90.66; H, 9.39.

6-Phenyl-1,3-hexadiene (29, Method B): IR (neat) 1650 (m), 1605, 1500, 1465, 1035 (m), 1008, 956, 905, 750, 704 cm^{-1}; NMR shows 85:15 E:Z ratio. E isomer: ^1H NMR ($CDCl_3$, 270 MHz) δ 2.39 (q, J = 7 Hz, 2 H), 2.70 (t, J = 7.5 Hz, 2 H), 4.96 (ddd, J = 10.11, 1.10, 0.6 Hz, 1 H), 5.08 (ddd, J = 16.73, 1.10, 0.6 Hz, 1 H), 5.72 (dt, J = 15.07, 6.99 Hz, 1 H), 6.07 (dd of pentuplet, J = 15.07, 10.30, 0.5–0.7 Hz, 1 H), 6.29 (dt, J = 16.73, 10.2 Hz, 1 H), 7.16 (m, 3 H), 7.26 (m, 2 H). The Z isomer showed the C_5 protons at 2.51 (q, J = 7.5 Hz), as well as completely exposed peaks at 5.17 (dd, J = 16.9, ~1.5 Hz), 5.47 (dt, J = 10.5, ~7.5 Hz), and 6.59 (dddd, J = 16.9, 11.2, 10.3, 1.1 Hz).

Anal. Calcd for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 91.15; H, 8.85.

1,3-Tetradecadien-5-yne (30, Method A). Alcohol **13** (1.21 g, 5.82 mmol) and Et_3N (1.71 mL, 12.2 mmol) in 10 mL of CH_2Cl_2 at 0 °C was treated with 2,4-dinitrobenzenesulfenyl chloride (1.44 g, 6.13 mmol). About 3 mg of bis(3-*tert*-butyl-4-hydroxy-5-methylphenyl) sulfide was added to inhibit radical polymerization. After 10 min at 0 °C and 30 min at 25 °C, 30 mL of pentane was added, the mixture was filtered, and the residue was rinsed with another 10 mL of pentane. The filtrates were shaken with 30 mL of aqueous $NaHCO_3$, dried, concentrated, and purified by bulb-to-bulb distillation (60–65 °C, 0.15 mmHg). The 65:35 E:Z mixture was separated by GC (20% SE-30 on Chromosorb W, 5 ft, 145 °C) to obtain pure samples of each isomer. The minor component, the Z isomer, eluted first: IR (neat) 2920, 2850, 2205 (w), 1460 (m), 1430 (m), 1000, 910, 785 (w), 665 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 0.88 (t, J = 7.1 Hz, 3 H), 1.28 (m, 8 H), 1.4 (m, 2 H), 1.56 (pent, J = 7 Hz, 2 H), 2.37 (td, J = 7.0, 2.2 Hz, 2 H), 5.26 (d, J = 9.0 Hz, 1 H), 5.33 (d, J = 18.0 Hz, 1 H), 5.45 (br d, J = 10.8 Hz, 1 H), 6.31 (t, J = 10.8 Hz, 1 H), 6.87 (dtd, J = 17.1, 10.5, 0.9 Hz, 1 H). The E isomer was the major component: IR (neat) 2925, 2860, 2150 (w), 1625 (w), 1460, 1005, 945, 910, 745 (w), 725 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 0.88 (t, J = 7.0 Hz, 3 H), 1.2–1.4 (m, 10 H), 1.50 (m, 2 H), 2.32 (td, J = 7.0, 2.2 Hz, 2 H), 5.12 (dd, J = 9.2, 1.4 Hz, 1 H), 5.24 (dd, J = 16.9, 1.4 Hz, 1 H), 5.61 (dt, J = 15.4, 1.5 Hz, 1 H), 6.34 (dt, J = 16.9, 10.7 Hz, 1 H), 6.50 (dd, J = 15.4, 10.7 Hz, 1 H).

Anal. Calcd for $C_{14}H_{22}$ (isomer mixture): C, 88.35; H, 11.65. Found: C, 88.25; H, 11.73.

4-Phenyl-1,3-pentadiene (31, Method A): bp ~60 °C (~15 mmHg) (lit. bp[34] 78–82 °C, (10 mmHg)); ^1H NMR δ 2.10 (s, 3 H), 5.08 (br d, J = 10 Hz), 5.20 (dd, J = 16, 2.5 Hz) total 2 H, 6.32 (br d, J = 11 Hz), 6.64 (ddd, J = 17, 11, 10 Hz) total 2 H, 7.0–7.3 (m, 5 H); MS 144.0939 (M^+), calcd for $C_{11}H_{12}$, 144.0939.

1-Bromo-4-phenyl-1,3-pentadiene (32, Method A): IR (neat) 1683 (w), 1615 (m), 1490, 1440, 1305, 940, 760, 700 cm^{-1}; ^1H NMR δ 2.20 (s), 2.25 (s) total 3 H, 6.0–7.1 (m, 3 H), 7.2–7.5 (m, 5 H); MS, m/e 222.0039 (M^+), calcd for $C_{11}H_{11}Br$, 222.0044. Detailed analysis of the 270-MHz NMR spectrum in $CDCl_3$ led to the tentative assignment of structure (*ZE*:*EE*:*ZZ* 6:3:1) and ^1H NMR properties shown.

1-Chloro-4-phenyl-1,3-pentadiene (33, Method A): MS, m/e 178.0544 (M^+), calcd for $C_{11}H_{11}Cl$, 178.0549. Detailed analysis of the 270-MHz

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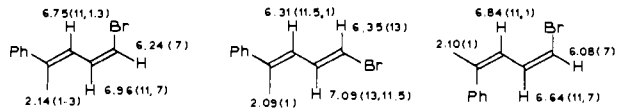
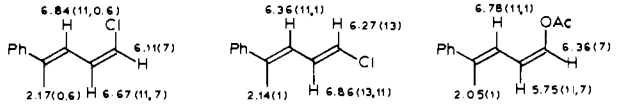


32-ZE 32-EE 32-ZZ

NMR spectrum ($CDCl_3$) including decoupling experiments led to the tentative assignment of structure (*ZE*:*EE* 2:1) and ^1H NMR chemical shifts and coupling constants shown.



33-ZE 33-EE 34-ZE

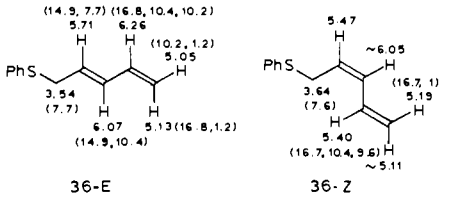
1-Acetoxy-4-phenyl-1,3-pentadiene (34). Dehydration of the alcohol **17** under the standard conditions of method A gave a single isomer (*ZE*) in 55% yield. NMR chemical shifts and couplings are given in the figure.

1-((Phenylsulfonyl)methyl)-1,3-cyclohexadiene (35, Method A). Alcohol **18** (3.11 g, 12.3 mmol) and pyridine (2.80 mL, 35.0 mmol) were cooled to 0 °C in 20 mL of CH_2Cl_2. 2,4-Dinitrobenzenesulfenyl chloride (3.43 g, 14.6 mmol) was added in portions over 3 min. After 10 min at 0 °C and 2 h at 25 °C, pentane (20 mL) was added. The mixture was filtered, the residue was rinsed with 40 mL of 1:1 CH_2Cl_2–pentane, and the filtrates were concentrated (~10 mg bis(3-*tert*-butyl-4-hydroxy-5-methylphenyl) sulfide was added to inhibit polymerization). Crystallization from ether–pentane gave ~0.8 g of white needles. Column chromatography of the mother liquors (25:75 ether–pentane) gave additional diene, for a total of 1.47 g (51%): mp 102.5–103 °C; IR (KBr) 1438, 1294, 1150, 1125, 1085, 750, 690, 600 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 2.18 (m, 4 H), 3.80 (br s, 2 H), 5.57 (br d, J ~ 5 Hz, 1 H), 5.8 (m, 2 H), 7.6 (m, 3 H), 7.9 (m, 2 H); MS 234.0714 (M^+), calcd for $C_{13}H_{14}O_2S$, 234.07144.

5-(Phenylthio)-1,3-pentadiene (36, Method B): Purified by TLC (10:90 ether–pentane, R_f 0.8): IR (neat) 1652 (w), 1488, 1444, 1010, 957, 912, 742, 695 cm^{-1}; ^1H NMR δ 3.45 (d, J = 6 Hz, 2 H), 4.9–5.2 (m, 2 H), 5.4–6.5 (m, 3 H), 7.1–7.4 (m, 5 H).

Anal. Calcd for $C_{11}H_{12}S$: C, 74.95; H, 6.86. Found: C, 74.76; H, 6.80.

A more careful examination of the 270-MHz NMR spectrum ($CDCl_3$) showed that the product was an 87:13 mixture of *E*:*Z* isomers, with the NMR properties shown.



36-E 36-Z

2-(1,3-Butadien-1-yl)-1,3-dithiane (37, Method B). To alcohol **20** (0.396 g, 2.08 mmol) and Et_3N (0.70 mL, 5.00 mmol) in 3 mL of ethylene dichloride were added 2,4-dinitrobenzenesulfenyl chloride (0.585 g, 2.49 mmol) and ~4 mg of bis(3-*tert*-butyl-4-hydroxy-5-methylphenyl) sulfide to inhibit polymerization. The mixture was refluxed for 45 min, then cooled to 25 °C, and diluted with 6 mL of pentane. After filtration and concentration of filtrates, the oil was eluted through 10 g of silica gel with 10:90 ether–pentane to give 0.22 g (61%) of the diene; ^1H NMR ($CDCl_3$, 270 MHz) δ 1.84 (m, 1 H), 2.1 (m, 1 H), 2.9 (m, 4 H), 4.67 (d, J = 7.4 Hz, 1 H), 5.14 (dd, J = 10.8, 1.2 Hz, 1 H), 5.25 (dd, J = 16.7, 1.2 Hz, 1 H), 5.75 (dd, J = 14.1, 7.4 Hz, 1 H), 6.3–6.4 (m, 2 H, decoupling experiments showed a signal at 6.3, ddd, J = 16.7, 10.8, 9.3 Hz, and 6.4, dd, J = 14.1, 9.3 Hz), in agreement with literature spectrum.[35]

2-(1,3-Butadien-1-yl)-2-(2-furyl)-1,3-dithiane (38, Method B). Purified by TLC (10:90, ether–pentane, R_f 0.5); ^1H NMR ($CDCl_3$, 270 MHz) δ 1.9 (m, 2 H), 2.8 (m, 4 H), 5.14 (dd, J = 9.9, 1.6 Hz, 1 H), 5.21 (dd, J = 16.7, 1.6 Hz, 1 H), 5.90 (d, J = 15.1 Hz, 1 H), 6.15 (dd, J = 15.1, 10.4 Hz, 1 H), 6.36 (~dt, J = 16.7, ~10 Hz, 1 H), 6.37 (dd, J = 3.1, 1.8 Hz), 6.55 (dd, J = 3.1, 0.9 Hz, 1 H), 7.45 (dd, J = 1.8, 0.9 Hz, 1 H).

4-Methyl-1-phenyl-2-cyclohexenols 42a and **43a** were obtained from 4-methylcyclohexenone[36] and PhLi as in the procedure for the preparation of **1a**. Workup and TLC (1:10:89 Et_3N–ether–pentane) gave, at R_f 0.2, 0.96 g (58%) of 1-phenyl-*trans*-4-methyl-2-cyclohexenol (**42a**). The compound was recrystallized in ether–pentane: mp 60.0–60.5 °C; ^1H NMR ($CDCl_3$, 270 MHz) δ 1.00 (d, J = 8 Hz, 3 H), 1.10 (m, 1 H), 1.70–2.00 (m, 3 H), 2.22 (m, 1 H), 2.60 (br s, 1 H), 5.60 (br d, J = 9.9 Hz, 1 H), 5.80 (dd, J = 9.9, 2.9 Hz, 1 H), 7.15–7.30 (m, 3 H), 7.43 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 20.59, 27.44, 29.81, 37.93 72.87, 125.76, 126.65, 127.69, 131.06, 135.48, 147.12; MS (M^+) 188.1200, calcd for $C_{12}H_{16}O$, 188.1201. At R_f 0.3, 0.23 g (14%) of 1-phenyl-*cis*-4-methyl-2-cyclohexenol (**43a**) was isolated: ^1H NMR δ 1.06 (d, J = 7 Hz, 3 H), 1.3–2.1 (m, 5 H), 2.23 (br s, 1 H), 5.7 (m, 2 H), 7.1–7.4 (m, 5 H). The assignment of the two isomers was confirmed by hydrogenation to the known saturated alcohols.[20]

1-Phenyl-*trans*-4-methyl-2-cyclohexen-1-ol (42a) (0.10 g, 0.54 mmol) was hydrogenated in 3 mL of 95% EtOH at 1 atm of H_2 for 25 min (1 equiv of H_2) with 52 mg of 5% rhodium on alumina. TLC (10:90 ether–pentane, R_f 0.2) gave 0.094 g (92%) of 1-phenyl-4-*trans*-methylcyclohexanol as a white crystalline solid: ^1H NMR ($CDCl_3$, 270 MHz) δ 0.902 (d, J = 6.6 Hz, 3 H), 1.1 (m, 2 H), 1.7 (m, 3 H), 1.8 (m, 2 H), 1.95 (br s, 1 H), 2.3 (m, 2 H), 7.3 (m, 3 H), 7.5 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 19.7, 29.76, 30.42, 36.22, 73.20, 125.54, 126.92, 128.24, 146.51.

1-Phenyl-*cis*-4-methyl-2-cyclohexen-1-ol (43a) (0.040 g, 0.21 mmol) was hydrogenated similarly to the trans methyl isomer to give 1-phenyl-4-*cis*-methyl-cyclohexanol: ^1H NMR ($CDCl_3$, 270 MHz) δ 0.970 (d, J = 5.5 Hz, 3 H), 1.4 (m, 3 H), 1.6 (m, 2 H), 1.8 (m, 5 H), 7.3 (m, 3 H), 7.5 (m, 2 H). The chemical shift of the methyl group in the trans isomer is reported[20] to be δ 0.90 (J = 6 Hz) and that in the cis isomer to be δ 0.98 ($W_{1/2}$ = 4 Hz).

1-(2,5-Dichlorophenyl)-4-methyl-2-cyclohexenol (42b and 43b). Prepared similarly to **1b** from 4-methyl-2-cyclohexenone and 2,5-dichloroiodobenzene.[21] TLC (20:80 ether–pentane) gave, at R_f 0.3, the trans methyl isomer **42b**, 1.30 g (51%), which was recrystallized from hexane; mp 71.5–72 °C; ^1H NMR ($CDCl_3$, 270 MHz) δ 1.07 (d, J = 6.6 Hz, 3 H), 1.16 (m, 1 H), 1.78 (ddd, J = 12.7, 9.0, 3.1 Hz, 1 H), 1.94 (m, 1 H), 2.33 (m, 1 H), 2.53 (ddd, J = 12.5, 9.6, 2.9 Hz, 1 H), 2.87 (br s, 1 H), 5.71 (br d, J = 9.9 Hz, 1 H), 5.94 (dd, J = 9.9, 3.3 Hz, 1 H), 7.18 (dd, J = 8.3, 2.4 Hz, 1 H), 7.28 (d, J = 7.2 Hz, 1 H), 7.63 (d, J = 4.2 Hz, 1 H); MS 256.0423 (M^+), calcd for $C_{13}H_{14}Cl_2O$, 256.0422.

Anal. Calcd for $C_{13}H_{14}Cl_2O$: C, 60.72; H, 5.49. Found: C, 60.70; H, 5.49.

The cis methyl isomer **43b** was obtained at R_f 0.4 and recrystallized from ether–pentane, yielding 0.100 g (3.9%) of white needles: mp 66.5–67.5 °C; ^1H NMR ($CDCl_3$, 270 MHz) δ 1.09 (d, J = 7.2 Hz, 3 H), 1.54 (m, 1 H), 1.75–1.87 (m, 2 H), 2.2–2.3 (m, 3 H), 5.66 (ddd, J = 9.9, 2.6, 1.5 Hz, 1 H), 5.85 (ddd, J = 9.8, 1.8, 0.9 Hz, 1 H), 7.15 (dd, J = 8.5, 2.6 Hz, 1 H), 7.24 (d, J = 8.8 Hz, 1 H), 7.84 (d, J = 2.2 Hz, 1 H); MS 256.0407 (M^+), calcd for $C_{13}H_{14}Cl_2O$, 256.0422.

Anal. Calcd for $C_{13}H_{14}Cl_2O$: C, 60.72; H, 5.49. Found: C, 60.73; H, 5.56.

1-(2,5-Dichlorophenyl)-4-methyl-1,3-cyclohexadiene. 1-(2,5-Dichlorophenyl)-*trans*-4-methyl-2-cyclohexenol (**42b**) (0.217 g, 0.85 mmol) and NEt_3 (0.250 mL, 1.79 mmol) were stirred in 15 mL of CH_2Cl_2. 2,4-Dinitrobenzenesulfenyl chloride (0.223 g, 0.95 mmol) was added, the suspension was stirred 1 h, and the solvent was removed. The residue was triturated with 3 × 2 mL of pentane and eluted through 5 g of silica gel with pentane. The diene was isolated in 75% yield (0.15 g): ^1H NMR δ 1.85 (s, 3 H), 2.2 (m, 2 H), 2.5 (m, 2 H), 5.74 (dq, J = 6, 1.5 Hz, 1 H), 5.92 (d, J = 6 Hz, 1 H), 7.0–7.3 (m, 3 H); MS 238.0314 (M^+), calcd for $C_{13}H_{12}Cl_2$; 238.0316.

1-(2,5-Dichlorophenyl)-3-(2,4-dinitrophenylsulfinyl)-*cis*-4-methyl-1-cyclohexene (44). The cis alcohol **43b** (0.043 g, 0.17 mmol) and Et_3N (0.030 mL, 0.22 mmol) were stirred under N_2 in 1.5 mL of CH_2Cl_2. 2,4-Dinitrobenzenesulfenyl chloride (0.043 g, 0.18 mmol) was added. After the solution stirred for 5 min, the suspension was filtered and the solvent was removed. TLC (35:65, ether–pentane, base line) gave 0.056 g (73%) of a yellow solid: mp 160–175 °C dec; IR (KBr) 1595, 1535, 1460 (m), 1345, 1090 (m), 1065 (m), 1045 (m), 1035 (m), 830 (m), 735 (m), 725 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 1.65 (d, J = 6.8 Hz, 3 H), 1.78 (dq, J = 14, 5 Hz, 1 H), 2.21 (m, 1 H), 2.46 (m, 3 H), 3.88 (br t, J = 4.5 Hz, 1 H), 4.87 (d, J = 4.1 Hz, 1 H), 7.17 (m, 2 H), 7.27 (d, J = 8 Hz, 1 H), 8.40 (d, J = 8.8 Hz, 1 H), 8.66 (dd, J = 8.6, 2.3 Hz, 1 H), 9.10 (d, J = 2.2 Hz, 1 H).

1-Phenylethyl 2-Nitrophenyl Sulfoxide (45). A solution of 0.206 g (1.14 mmol) of 2-nitrophenylthiocyanate and 0.117 mL (0.97 mmol) of 1-phenylethanol in 2 mL of CH_2Cl_2 was cooled to 0 °C, and 0.285 mL (1.14 mmol) of tri-*n*-butylphosphine was added dropwise. After 10 min,

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(35) Seebach, D.; Kolb, M. *Liebigs Ann. Chem.* **1977**, 811.
(36) Using the method of: Garbisch, E. W., Jr. *J. Org. Chem.* **1965**, *30*, 2109.

the bath was removed and stirring was continued for 20 min. Solvent was removed, and the product was purified by chromatography on silica gel (1:9 ether–pentane) to give, after recrystallization from ether–pentane, 0.212 g (83%) of 1-phenylethyl 2-nitrophenyl sulfide: mp 90.5–91.5 °C; ^{1}H NMR δ 1.70 (d, J = 7 Hz, 3 H), 4.47 (q, J = 7 Hz, 1 H), 7.1–7.4 (m, 8 H), 7.98 (d, J = 8 Hz, 1 H).

Anal. Calcd for $C_{14}H_{13}NO_2S$: C, 64.84; H, 5.05. Found: C, 64.81; H, 5.00.

The sulfide prepared above (67 mg, 0.259 mmol) in 15 mL of CH_2Cl_2 was cooled to 0 °C, and 52 mg (0.258 mmol) of *m*-chloroperbenzoic acid was added. After 10 min, the reaction mixture was filtered through Celite, and solvent was removed from the filtrate. Crystallization from CH_2Cl_2–pentane gave 54.7 mg (77%) of **45** as yellow needles: mp 98–99 °C; ^{1}H NMR ($CDCl_3$, major diastereomer, 3:1 ratio) δ 1.36 (d, J = 7 Hz, 3 H), 4.28 (q, J = 7 Hz, 3 H), 7.3–7.6 (m, 5 H), 7.67 (t m, J = 8 Hz, 1 H), 7.93 (t m, J = 8 Hz, 1 H), 8.24 (d m, J = 8 Hz, 1 H), 8.27 (d m, J = 8 Hz, 1 H).

The elimination rate was measured in $CDCl_3$ solution (0.2 M) containing 0.4 M Et_2NH at 38 °C in the NMR probe, k = (1.39 ± 0.09) × 10^{-5} s^{-1}.

1-Phenylethyl 2,4-dinitrophenyl sulfoxide (46) was prepared by a procedure similar to one above. Sulfide: mp 109–110 °C; IR 1590, 1535, 1518, 1355, 1340, 1055, 740, 705 cm^{-1}; ^{1}H NMR δ 1.68 (d, J = 7 Hz, 3 H), 4.60 (q, J = 7 Hz, 1 H), 7.2–7.6 (m, 6 H), 8.13 (dd, J = 9, 2 Hz, 1 H), 8.80 (d, J = 2 Hz, 1 H); MS 304.0511 (M^+), calcd for $C_{14}H_{12}N_2O_4S$, 304.0523. Sulfoxide (**46**): ^{1}H NMR ($CDCl_3$, partial) δ 4.25–4.3 (br q, J = 6 Hz), 8.65 (d, J = 8 Hz), 8.96 (s). Decomposed in $CDCl_3$ to styrene at 38 °C, k = 1.34 × 10^{-4} s^{-1}.

Acknowledgment. We thank the National Science Foundation and the Wisconsin Alumni Research Foundation for support of this work.

Registry No. 1a, 83333-70-4; **1b**, 68099-13-8; **1c**, 60174-90-5; **2a**, 83333-71-5; **2b**, 68099-15-0; **2c**, 15619-32-6; **4**, 68099-18-3; **5a**, 17488-64-1; **5b**, 68099-38-7; **6**, 31952-17-7; **7**, 32363-86-3; **8**, 68099-17-2; **9**, 68099-19-4; (*E*)-**10**, 68099-20-7; (*E*)-**11** (isomer 1), 83333-72-6; *E*-**11** (isomer 2), 83334-14-9; (*E*)-**12**, 83333-73-7; (*Z*)-**12**, 83334-11-6; (*E*)-**13**, 83333-74-8; (*E*)-**14**, 83333-75-9; (*E*)-**15**, 83333-76-0; (*E*)-**16**, 83333-77-1; (*E*)-**17**, 83333-78-2; **18**, 83333-79-3; (*E*)-**19**, 5284-13-9; (*E*)-**20**, 83333-80-6; (*E*)-**21**, 83333-81-7; **22a**, 68099-24-1; **22b**, 68099-25-2; **22c**, 83333-82-8; **23a**, 15619-34-8; **24**, 83333-83-9; **25**, 21473-05-2; **26**, 57293-43-3; (*E*)-**27**, 68099-28-5; (*Z*)-**27**, 83334-03-6; (*E*,*E*)-**28**, 68099-29-6; (*E*,*Z*)-**28**, 68099-40-1; (*E*)-**29**, 77605-16-4; (*Z*)-**29**, 77605-17-5; (*E*)-**30**, 83333-84-0; (*Z*)-**30**, 83334-04-7; (*E*)-**31**, 55177-38-3; (*Z*,*E*)-**32**, 83333-85-1; (*E*,*E*)-**32**, 83334-12-7; (*Z*,*Z*)-**32**, 83334-13-8; (*E*,*E*)-**33**, 83333-86-2; (*Z*,*E*)-**33**, 83334-05-8; (*Z*,*E*)-**34**, 83333-87-3; **35**, 83333-88-4; (*E*)-**36**, 83333-89-5; (*Z*)-**36**, 83334-06-9; (*E*)-**37**, 83333-90-8; (*Z*)-**37**, 83334-07-0; (*E*)-**38**, 83333-91-9; **40** (isomer 1), 83333-92-0; **40** (isomer 2), 83333-93-1; **42a**, 83333-94-2; **42b**, 83333-95-3; **43a**, 83333-96-4; **43b**, 83333-97-5; **44**, 83333-98-6; **45**, 83333-99-7; **46**, 83334-00-3; PhLi, 591-51-5; 4-methyl-2-nitrobenzeneselenenyl chloride, 68099-14-9; 4-methyl-2-nitrophenylselenocyanate, 65275-29-8; 4-methyl-2-nitrophenyl methyl selenide, 83334-01-4; 2-iodotoluene, 615-37-2; 2-cyclohexenone, 930-68-7; prenyl phenyl selenide, 69690-81-9; 1-bromo-3-phenylpropane, 637-59-2; butyl phenyl selenide, 28622-61-9; 2-phenylpropionaldehyde, 93-53-8; propenyl bromide, 590-14-7; 1-decyne, 764-93-2; crotonaldehyde, 4170-30-3; 2-phenyl-3-penten-2-ol, 4743-67-3; 4-bromo-3-phenyl-2-pentanone, 83334-02-5; allyl phenyl selenide, 14370-82-2; acetophenone, 98-86-2; phenyl (4-phenyl-1-penten-4-ol-3-yl) selenide, 83334-08-1; phenyl (4-phenyl-2-penten-4-ol-1-yl) selenide, 83334-09-2; 4-phenyl-2-pentene-1,4-diol, 83334-10-5; 2,4-dinitrobenzenesulfenyl chloride, 528-76-7; 1-phenyl-4-*trans*-methylcyclohexanol, 30689-84-0; 1-phenyl-4-*cis*-methylcyclohexanol, 30689-83-9; 4-methylcyclohexenone, 5515-76-4; 2,5-dichloroiodobenzene, 29682-41-5; 4-methyl-2-cyclohexenone, 5515-76-4; 2-nitrophenylthiocyanate, 2769-30-4; 1-phenylethanol, 98-85-1; 1-phenylethyl 2-nitrophenyl sulfide, 19758-58-8.

Supplementary Material Available: Spectroscopic data and/or experimental details for the preparation of the following compounds: 2,4-dinitrobenzeneselenocyanate, 2,4-dinitrobenzeneselenenyl bromide, **1c**, **4**, **6**, **8**, **9**, **14**, **18**, **19**, **20**, **21**, **40**, and **41** (5 pages). Ordering information is given on any current masthead page.

Induced Circular Dichroism of β-Cyclodextrin Complexes with Azanaphthalenes—Polarization Directions of the $\pi^* \leftarrow \pi$ Transitions in Azanaphthalenes

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Contribution from the Chemical Research Institute of Non-aqueous Solutions, Tohoku University, Sendai 980, Japan. *Received August 17, 1981*

Abstract: The induced circular dichroism (ICD) spectra of the β-cyclodextrin (β-CD_x) complexes with mono-, di-, and triazanaphthalenes were measured in the wavelength region 200–400 nm. The polarization analysis and spectral assignments of these azanaphthalenes were made from the comparison of the theoretical results calculated by using the CNDO/S-CI approximation with the observed ICD spectra. The polarization directions of the first $\pi^* \leftarrow \pi$ transitions in azanaphthalenes are closely related to the position of aza nitrogen atoms and can be determined by the coefficients of the configurations in the corresponding lowest $\pi^* \leftarrow \pi$ states. From the observation of the ICD band with mixed signs, the presence of the "forbidden" character is strongly suggested in the second absorption bands of isoquinoline, phthalazine, cinnoline, and quinazoline. In each case of azanaphthalenes, the observation of positive ICD bands in the third absorption band indicated the predominance of the long-axis-polarized electronic transitions.

Polarization analysis is one of the most useful techniques for spectral assignments of aromatic compounds, since it offers information on the transition-moment directions and vibronic structure. The measurements of polarized or linear dichroism[1] spectra require a partially oriented assembly of molecules achieved by the preparation of single and mixed crystals,[2,3] the dispersion of solute molecules in nematic liquid crystal[4] and stretched polymer sheet,[5-7] the application of electric or magnetic fields[8,9] and hy-

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(1) Linear dichroism is defined as the difference in absorbance found when linearly polarized light with the electric vectors in two directions, perpendicular to each other, is used. (a) B. Norden, *Appl. Spectrosc. Rev.*, **14**, 157 (1978); (b) E. W. Thulstrup, "Aspects of the Linear and Magnetic Circular Dichroism of Planar Organic Molecules", Springer-Verlag, Berlin, 1980.

(2) D. S. McClure, *J. Chem. Phys.*, **22**, 1668 (1954); **24** 1 (1956); **25**, 481 (1956); J. W. Sidmann and D. S. McClure, *ibid.*, **24**, 757 (1956).

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