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 \( pK_a \leq 10 \) are secondary or tertiary alcohols except for the acetoxyhydroxamate anion. The change in slope corresponds to a change in the value of \( \beta_{10} \) 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 acetohydrate, but a clear conclusion is not possible.

The limiting magnitudes of \( \beta_{40} \) and \( \beta_{10} \) for formation of an anionic addne intermediate are expected to be similar: the limiting values of \( \beta_{40} \) and \( \beta_{10} \) are approximately 0.8 and -0.9, respectively, from a value of \( \beta_{10} \) = 1.0 and \( \beta_{40} \) = 0.7 for the formation of an uncharged intermediate 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).

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

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Conversion of Allyl Alcohols to 1,3-Dienes by Sequential Sulfenate–Sulfoxide [2,3] Sigmatropic Rearrangement and Syn Elimination

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Abstract: A method for the 1,4 dehydroxylation 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 dehydroxylation was shown to occur with overall cis stereochemistry in a cyclic system, consistent with the postulated mechanism. The dehydroxylation can also be performed with selenenyl halides, but conditions are more severe, and the reaction is less general than with 2,4-dinitrobenzenesulfonyl chloride.

The dehydroxylation 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. In addition to treatment with catalytic amounts of sulfonic acids, Burgess reagent, pyrolysis over aluminia, acetate

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Scheme 1

This conclusion is consistent with the observation that there is little or no change in the secondary \( \alpha \) or \( \beta \) 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. In particular, the secondary \( \alpha \)-deuterium isotope effect of \( k_D/k_H = 1.22 \) for the attack of a series of phenolate and alkoxide ions on p-nitrobenzyl formate is large and constant, suggesting that there is a considerable amount of bond formation and little change in the structure of the transition state for these nucleophiles. Similarly, the \( p_p \) 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 \( p_p = 0.07 \). This work provides additional support for the conclusions (1) that observed \( \beta \) values for basic oxygen anions do not provide a reliable measure of the amount of bond formation or cleavage in the transition state and (2) that curved structure-reactivity plots for reactions involving these anions do not necessarily represent changes in transition-state structure.

---


(51) The limiting magnitudes of \( \beta_{40} \) and \( \beta_{10} \) for formation of an anionic addne intermediate are expected to be similar: the limiting values of \( \beta_{40} \) and \( \beta_{10} \) are approximately 0.8 and -0.9, respectively, from a value of \( \beta_{10} \) = 1.0 and \( \beta_{40} \) = 0.7 for the formation of an uncharged intermediate 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).

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Registry No. D.O, 7789-20-0; (CF₃)₂(OH), 677-71-4; (CHF₃)₂C(O-H)₂, 518-45-6; (CF₃)₂CHOH, 920-66-1; (CF₃)(CF₂)C(OH)₂, 421-76-1; (CF₃)₂COH, 2378-02-1; p-nitrophenyl acetate, 830-03-5; 2,4-dinitrophenyl acetate, 4232-27-3; 1-acetoxy-4-methoxypridinium ion, 46123-02-8; 1-acetoxy-4-methoxypridinium perchlorate, 19921-03-0.


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

An alternative to a direct dehydration would be a regiospecific transformation 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 efforts along these lines have 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 sulfides have been elegantly elucidated in studies by Mislow and co-workers. 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. Numerous synthetic applications of these rearrangements have been reported. However, until this time this investigation was begun, there were no reports in the literature of eliminations of allylic sulfenates to form 1,3-dienes specifically. In fact, both α-methylallyl14 and α,α-dimethylallyl15 sulfoxides have been reported to undergo a [1,3] sigmatropic shift in preference to syn elimination.16 It is for this reason and the fact that selenoxide syn eliminations proceed at approximately 100 °C lower temperature than those of sulfides that we began our work by investigating the applicability of Scheme I with Y = Se.

The chemistry and thermodynamics of allylic selenides and their [2,3] sigmatropic rearrangement products, the allylic selenenates, are much less well studied than the sulfur analogues. Allylic selenenates are generally unstable even well below room temperature, and the intermediacy of the allyl selenenate esters is at best poorly understood, although the stoichiometric reaction, as we will describe below, does work well.

We began our investigation by treating 1-(o-tolyl)-2-cyclohexenol (1a) with a series of selenenyl and sulfenyl halides. 2,4-Dinitrobenzenesulfenyl 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 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 dehydrogenation using 2,4-dinitrobenzenesulfonyl 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-unsatuated ketones and aldehydes—the organometallic reagents used (compound formed) are phenylmethylsilane (C≡C), (4, 9, 14, 42a, 43a), o-tolyllithium (1a), 2,5-dichlorophenylmethyl lithium (1b, 42b, 43b), dicyclopentadienyl lithium (1c), 1-propanesulfonylethylene bromide (1d), phenylsulfonylmethylmethylmethyl (1e), phenylthio-methyl lithium (1f), α-(phenylsulfonyl)methylmethyl (1g), 2-lithiodithiane (1h, 42a, 43b), and 2-(2,2-dinitrophenyl)-2-lithiodithiane (1i) (b) alkylolation or hydroxyalkylation of a metallated allylic phenyl selenide, followed by oxidation of the selenide (10, 17); (c) reaction of α-lithioalkyl phenyl selenoxides with aldehydes, followed by selenoxide syn elimination (11, 12); (d) acid-catalyzed allylic rearrangement of allyl alcohols (5a, 5b); (e) reduction of α,β-unsatuated ketones (6, 8); (f) miscellaneous transformations of allyl alcohols (15, 16, 41); (g) allylic oxidation (7).

1.4 Dehydrogenations of Allyl Alcohols. To test the scope of the preparation of dienes according to the method of Scheme I using

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Footnotes:


Conversion of Allyl Alcohols to 1,3-Dienes


Table 1. Diene Formation from Allyl Alcohols According to Scheme I (Ar-Y-X = 2,4-Dinitrobenzenesulfonyl Chloride, 3)

<table>
<thead>
<tr>
<th>NO</th>
<th>ALLYL ALCOHOL</th>
<th>NO</th>
<th>DIENE</th>
<th>YIELD</th>
<th>E/Z</th>
</tr>
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<tr>
<td>1a</td>
<td>Ar = 2-Ch3C6H3</td>
<td>2a</td>
<td>2b</td>
<td>68b</td>
<td>79</td>
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<td>1b</td>
<td>2.5-ClC6H3</td>
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</tr>
<tr>
<td>4</td>
<td>Ph+</td>
<td>22a</td>
<td>22b</td>
<td>75</td>
<td></td>
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<tr>
<td>5a</td>
<td>Ar = 2-Ch3C6H3</td>
<td>23a</td>
<td>23b</td>
<td>71</td>
<td>10</td>
</tr>
<tr>
<td>5b</td>
<td>2.5-ClC6H3</td>
<td>23c</td>
<td></td>
<td></td>
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<tr>
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<td>25a</td>
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</tr>
<tr>
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<td>73</td>
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<tr>
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<tr>
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<td>37a</td>
<td></td>
<td>61</td>
<td>75/8</td>
</tr>
<tr>
<td>21</td>
<td>Ph+</td>
<td>38a</td>
<td></td>
<td>62</td>
<td></td>
</tr>
</tbody>
</table>

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

2,4-dinitrobenzenesulfonyl chloride (3), we subjected a variety of alcohols to our optimized conditions (1.05–1.10 equiv of 3, 2.3 equiv of Et3N) 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 ArS-X species by diluting the reaction mixture with pentane, followed by filtration, which removes most of the insoluble sulfur-containing materials (ArSCI, 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-cyclohexadienies (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 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 C2,3 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 diene under various conditions (triethylamine, pyridine, or sodium hydride as base). The sulfenyl chloride may be attacking the sulfur19 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.

On the basis of previous results in our laboratory and others\(^\text{19}\) 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, disopropylethylamine 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 \((E:Z = 74:26 \text{ and } 15:85)\), 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 stereochromy 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 \(\beta\)-olefinic proton and the allylic proton adjacent to it. In the trans alcohol the dihedral angle between the protons is small \((\sim 10-15^\circ)\) and the coupling constant is larger than that in the cis isomer \((43a, < 1 \text{ Hz}; 43b, 1.8 \text{ Hz})\), 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 \((42a\text{ and }43a)\) 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\text{-di-tert-butyl-}

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 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 ArSCI-Et\(_3\)N-CH\(_2\)Cl\(_2\), 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 \(\delta \sim 5.66 \text{ and } 5.85\) and the appearance of new protons at \(\delta \sim 4.88 \text{ and } 3.90\) \((\text{the chemical shifts of the } 2,5\)-dichlorophenyl group are similar to those in 4b and 4b 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 \(\sim 1000-1100 \text{ cm}^{-1}\) was particularly weak \((\text{as compared with other vibrational modes of the molecule})\). The material could not be purified sufficiently for an elemental analysis.

These results, together with those of Rapoport and co-workers\(^\text{6}\) 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\(^\text{22}\) and the allylic nature of the sulfoxide (in analogy with benzylic selenoxides\(^\text{16}\)). These effects are illustrated for two benzylic sulfoxides \((45 \text{ and } 46)\) that show first-order elimination rates of \(k = 1.39 \times 10^{-3} \text{ s}^{-1}\) for 45 and \(k = 1.3 \times 10^{-4} \text{ s}^{-1}\) for 46 at 38 °C. For comparison, 1-phenylethyl phenyl selenoxide \((47)\) has \(k \gtrsim 1.5 \times 10^{-4} \text{ s}^{-1}\).
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-sulfenate 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 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, α-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-dinitrobenzenesulfonyl 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 16 h at 25 °C. Diene formation in the former case represents the first demonstration of reversibility of the allyl selenenate rearrangement.24 That the difficulty 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.25

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.26 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.27

**Conclusions**

The simple procedure developed here has been shown to cleanly give a net 1,4 dehydrogenation 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 selenenate halides to the 1,4 dehydrogenation of allyl alcohols is severely limited since the [2,3] sigmatropic selenoxide–selenenate equilibrium is too strongly shifted toward the latter.25

**Experimental Section**

**General Procedures.** Nuclear magnetic resonance spectra were obtained on a JEOI MH-100 in CCl₄ 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 AEI MS-902 spectrometer. Preparative thin-layer chromatography was carried out with Merck PF-254 or NM-Kieselgel 60, UV light. 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.

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

<table>
<thead>
<tr>
<th>no.</th>
<th>mmol ArSCl</th>
<th>mmol</th>
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<th>method</th>
<th>reaction</th>
<th>yield, g (%)</th>
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2a, 2,4-Dinitrobenzenesulfonyl chloride. **b** (Method A) ArSCl added to a chilled solution of alcohol and base in CH₂Cl₂ (1.0–5.5). After 5 min, solution 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 CH₂Cl₂. **f** See ref 21. **g** Unrecrystallized ArSCl used. See ref 17. **h** Pyridine used as base. **i** Ethylidiosipropylamine used as base.

(23) 2-Cyclohexenyl 2,4-dinitrobenzenesulfinyl chloride is reported to be quite stable. Zel'rov, 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.


Table II gives experimental conditions for diene formation. The yields reported are for compounds to whose purity, as established by NMR spectroscopy, were known to be greater than 95% unless otherwise indicated.

4-Methyl-2-nitrobenzeneselenenyl chloride was prepared from the selenocyanate via the methyl selenide. The selenide was prepared by slow addition of NaBH₄ (0.200 g, 5.26 mmol) to a suspension of 4-methyl-2-nitrobenzeneselenenyl cyanate (1.23 g, 5.10 mmol) in 20 mL of 95% EtOH under N₂. After 20 min, the mixture was filtered and the suspension stirred for 2 h. The selenide was then taken up in ether and washed with 1.2 N HCl, aqueous NaHCO₃, and saturated aqueous NaCl, dried, and concentrated to give 1.01 g of 4-methyl-2-nitrobenzeneselenenyl chloride; mp 63.5-64.5 °C (lit. mp 65-67 °C).

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 solution was added dropwise to 0.458 mL (2.5 mmol) of pentane and then ether gave 0.385 g (97%) of the rearranged alcohol 5a, mp 79.0-80.0 °C; IR (CDC₁₃) ν 3400 (br), 2980, 2935, 1500, 1460, 1380, 1378, 1150, 850 cm⁻¹; IH NMR (CDCl₃) δ 1.5-2.0 (m, 7 H), 2.2 (m, 7 H), 4.30 (m, 1 H), 5.66 (dt, J = 15.1, 6 Hz). The yield of the selenide was 45% of the alcohol 5a.

2-Methyl-7-phenyl-3-buten-2-ol (5a). Alcohol la (0.398 g, 2.29 mmol) and p-toluenesulfonic acid (0.021 g, 0.11 mmol) were stirred in 5 mL of ether for 20 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 (CDCl₃) ν 3400 (br), 2980, 2935, 1500, 1460, 1380, 1378, 1150, 850 cm⁻¹; IH NMR (CDCl₃) δ 1.5-2.4 (m, 7 H), 2.48 (s, 3 H), 7.45 (br d, J = 6.5 Hz, 2 H), 7.2-7.4 (m, 5 H); MS m/e 242.0265, calcd for Cl₂HI₂Cl₂O, 242.0265.

2-Tetradecen-5-yn-4-ol (13). MeLi (1.38 M, 8.8 mmol) was slowly added to 1-decylene (0.108 g, 8.7 mmol) in THF at 0 °C. After 20 min, the solution was cooled to -78 °C and crotonaldehyde (0.655 mL, 9.7 mmol) in 20 mL of 95% EtOH was added. After 15 min, the solution was stirred at 0 °C for 30 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 112-113 °C; 1H NMR (CDCl₃) δ 1.5-2.4 (m, 7 H), 2.48 (s, 3 H), 7.45 (br d, J = 6.5 Hz, 2 H), 7.2-7.4 (m, 5 H); MS m/e 208.1822, calcd for C₁₃H₂₃O, 208.1827.

2-Chloro-3-phenylpent-2-en-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 CCl₄ under a sunlamp for 45 min. Filtration and TLC (1:95 EtOAc/ether, R₅ 0.15) gave 0.665 g (62%) of the brominated allyl alcohol: IR (neat) 3550 (br), 2980, 1715, 1515, 1470 (m), 1323 (m), 1280 (m), 1110 (m) cm⁻¹; IH NMR (CDCl₃) δ 1.5-3.7 (m, 6 H), 5.66 (d, J = 15.1, 6 Hz). The yield of the selenide was 85% of the alcohol 5a.
Dehydration Procedures. The reaction conditions for dehydration of the alcohols using 2,4-dinitrobenzenesulfonyl chloride are shown in Table II. (CAUTION—the formation of the sulfenate esters is exothermic; ArSCI 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 NET3), 35 (method A using pyridine), 37, 39 (method B), and 22 (method C). Preparation of compound 2b is described by use of 2-nitro-4-methylbenzenesulfonyl chloride.

1-(2-Methylphenyl)-1,3-cyclohexadiene (23a, Method A): 1H NMR δ 2.25 (s, 3 H), 4.05 (m, 2 H), 6.39 (br, 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.32

1,2-Dimethyl-1,3-cyclohexadiene (24a, Method B): 1H NMR δ 1.18 (t, J = 7.1 Hz, 3 H), 1.30 (quintet, J = 6.9 Hz, 2 H), 2.39 (quartet, J = 7.0 Hz, 2 H), 3.82 (dd, J = 11.6, 7.0 Hz, 2 H) and 6.51 (dddd, J = 9.0, 6.8, 5.4 and 3.7 Hz, 2 H). Anal. Calcd for C10H12: C, 88.35; H, 11.65. Found: C, 88.25; H, 11.73.

6-Phenyl-2,4-heptadiene (28, Method B). Elution of the crude product through silica gel (~5 g) with pentane 54% of the diene as a 65:35 mixture of two isomers, which were separated by TLC on 8% Al2O3 as the plate eluted with 2-nitro-4-methylbenzenesulfonyl chloride. The major isomer (R0.82) was (E,E)-6-phenyl-2,4-heptadiene: 1H NMR (CDCl3, 270 MHz) δ 1.26 (d, J = 7.0 Hz, 3 H), 1.59 (d, J = 6.2 Hz, 3 H), 3.34 (dd, 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 (R0.65) was (Z,E)-6-phenyl-2,4-heptadiene: 1H NMR (acetone-d6, 270 MHz) δ 1.35 (d, J = 7.0 Hz, 3 H), 1.48 (ddd, J = 10.1, 7.1 and 2.4 Hz, 2 H), 1.59 (m, 2 H), 2.19 (dd, J = 16.1 and 10.7 Hz, 1 H), 2.48 (dd, J = 10.7 and 7.1 Hz, 1 H), 2.60 (m, 2 H), 3.3 (m, 2 H), 6.29 (d, J = 10.7 Hz, 1 H), 6.59 (m, 1 H), 6.64 (dd, J = 15.3, 11.0 Hz, 1 H), 7.2 (m, 5 H).


1,3,4-Tetradeca-5-yn-10-one (30, Method A). Alcohol 13 (2.11 g, 5.82 mmol) and Et3N (1.71 mL, 12.2 mmol) in 10 mL of CH2Cl2 at 0°C was treated with 2,4-dinitrobenzenesulfonyl chloride (1.44 g, 6.13 mmol). About 3 mg of bis(3-tert-butyli-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 mixed with another 10 mL of pentane. The filtrates were shaken with 30 mL of aqueous NaHCO3, 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) 2925, 2850, 2205 (w), 1460 (m), 1430 (m), 1000, 915, 875 (w), 665 (cm−1); 1H NMR (CDCl3, 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 = 16.8 Hz, 1 H), 5.45 (br, J = 10.8 Hz, 1 H), 5.71 (d, J = 10.8 Hz, 1 H), 5.87 (d, J = 10.8 Hz, 1 H), 6.78 (dd, J = 17.1, 10.5 Hz, 1 H), 7.15 (m, 5 H). The E isomer was the major component: IR (neat) 2925, 2860, 2150 (w), 1625 (w), 1460, 1005, 945, 825 (w), 725 (cm−1); 1H NMR (CDCl3, 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), 5.41 (d, J = 14.7 Hz, 1 H), 5.61 (d, J = 10.8 Hz, 1 H), 6.72 (d, J = 16.9, 10.7 Hz, 1 H), 6.50 (dd, J = 15.4, 10.7 Hz, 1 H). Anal. Calcd for C15H12: C, 91.08; H, 8.92. Found: C, 91.15; H, 8.85.

1-Chloro-4-phenyl-1,3-pentadiene (31, Method A): bp ~ 60°C (~15 mmHg) (lit. bp17-78-82°C, 10 mmHg); 1H NMR δ 2.10 (s, 3 H), 5.08 (br, d, J = 10 Hz, 1 H), 5.20 (dd, J = 16, 2.5 Hz) total 3 H, 7.32 (br, d, J = 11 Hz, 1 H), 6.64 (dddd, J = 17.1, 11.0 Hz, 2 H) total 2 H, 7.0-7.3 (m, 5 H), MS: m/e 222.0309 (M+), calcd for C10H8Cl, 222.0309. Detailed analysis of the 270-MHz NMR spectrum in CDCl3 led to the tentative assignment of structure (Z/E/E/E: 63:1) and 1H NMR properties shown.

1-Chloro-4-phenyl-1,3-pentadiene (33, Method A): MS: m/e 178.0544 (M+), calcd for C10H7Cl, 178.0549. Detailed analysis of the 270-MHz

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 CH₂Cl₂. 2,4-Dinitrobenzenesulfenyl chloride (0.585 g, 2.49 mmol) and -4 mg of 2,4-dinitrobenzenesulfenyl chloride (0.043 mL, 0.22 mmol) were stirred under N₂ in 1.5 mL of CH₂Cl₂. 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 (3.9%) of white needles: mp 71.5-72 °C; 'H NMR (CDCl₃, 270 MHz) 6 1.06 (d, J = 6 Hz, 2 H), 1.57 (d, J = 2 Hz, 3 H), 7.1-7.4 (m, 3 H); MS 256.0423 (M⁺), calcd for C₁₃H₁₂Cl₂O: 256.0422 (M⁺).

Workup and TLC (1:10:89 Et₃N-ether-pentane) gave, at Rₚ 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; 'H NMR (CDCl₃, 270 MHz) 6 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 Hz, 1 H), 5.80 (dd, J = 9, 2.9 Hz, 1 H), 7.15-7.30 (m, 3 H), 7.43 (m, 2 H). 'H NMR (CDCl₃, 270 MHz) 6 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). 'H NMR (CDCl₃) 6 17.9, 27.0, 34.2, 36.2, 72.0, 125.5, 126.9, 128.4, 146.5. 1-Phenyl-cis-4-methyl-2-cyclohexenol (43a) (0.040 g, 0.21 mmol) was hydrogenated similarly to the trans methyl isomer to give phenyl-cis-4-methyl-cyclohexanol: 'H NMR (CDCl₃, 270 MHz) 6 0.970 (d, J = 6 Hz, 2 H), 1.1 (m, 2 H), 1.7 (m, 3 H), 7.5 (m, 2 H). The chemical shift of the methyl group in the trans isomer is reported to be 0.90 (J = 6 Hz) and that in the cis isomer to be 0.98 (W 1/2 = 4 Hz).

2-(1,3-Butadien-1-yl)-1,3-dithiane (36, Method B). To alcohol 20 (0.396 g, 2.08 mmol) and Et₃N (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 0 °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 (75%) of the diene; 'H NMR (CDCl₃, 270 MHz) 6 1.84 (m, 1 H), 2.1 (m, 1 H), 2.9 (m, 2 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 6.33, d, J = 16.7, 10.8, 9.3 Hz, and 6.4, dd, J = 14.1, 9.3 Hz), in agreement with literature spectrum. 22

2-(1,3-Butadien-1-yl)-1,3-dithiane (36, Method B). Purified by TLC (10:90 ether-pentane, Rₚ 0.5); 'H NMR (CDCl₃, 270 MHz) 6 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 (dd, J = 15.1, 10.4 Hz, 1 H), 6.36 (dd, J = 3.1, 1.8 Hz, 1 H), 6.55 (dd, J = 3.1, 0.9 Hz, 1 H), 7.45 (dd, J = 1.8, 0.9 Hz, 1 H).

1-Methyl-1-phenyl-2-cyclohexenols 42a and 42a were obtained from 4-methylcyclohexene and PhLi as in the procedure for the prepara-

Induced Circular Dichroism of β-Cyclodextrin Complexes

with Azanaphthalenes—Polarization Directions of the \( \pi^* \leftrightarrow \pi \) 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 \( \beta \)-cyclodextrin (\( \beta \)-CD) complexes with mono-, \( \delta \)-, and triazanaphthalenes were measured in the wavelength range 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 \( \pi^* \leftrightarrow \pi \) 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 expression of Planar Organic Molecules"}, Springer-Verlag, Berlin, 1980.

(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.


Preparation of Single and Mixed Cyanate Crystals, the Dispersion of Solute Molecules in Nematic Liquid Crystal4 and Stretched Polymer Sheet2,3 the Application of Electric or Magnetic Fields4,5 and Hydration of Solutes in Aqueous Solution6.