kinetic product in the reduction reaction is PPN⁺[CpV-(CO)₃Br]⁻. Assuming the photolysis proceeds via coordinatively unsaturated CpV(CO)₃, which reacts more quickly with PPh₃ than with Br⁻, we conclude that the same intermediate (which appears in mechanism IIIb) *cannot* be involved in the reduction. *Thus, the bromine atom must be transferred directly from carbon to metal* during the reduction reaction.[18]

The chain mechanism IIIa provides the most reasonable way of accounting for the data discussed above. We have encountered only one system which appears to act anomalously: the reduction of cyclopropylcarbinyl bromide (**11a**). In THF, this halide gives significant amounts of *both* methylcyclopropane (33%) and 1-butene (67%). The ring-opening rate constant for cyclopropylcarbinyl radical has been estimated[19] as ~1.0 × 10⁸ s⁻¹ at 25 °C; thus much less than 33% methylcyclopropane should be formed under our reaction conditions. Furthermore, although there is somewhat more scatter in the data than we observe with **3b**, the 1-butene/methylcyclopropane ratio is essentially *independent* of the vanadium hydride concentration. Although no difference in the **6b/7b** ratio is observed between reduction of bromide **3b** and iodide **3a**, cyclopropylcarbinyl iodide gives much more 1-butene (95%) than does the corresponding bromide. Most important, cyclopropylcarbinyl tosylate is reactive toward **1** *and gives >95% methylcyclopropane*. We conclude that a different mechanism must intervene in the case of **11**. It seems likely that the radical process oper-

$$\triangleright\!-\!CH_2\!-\!X \xrightarrow{\ [CpV(CO)_3H]^-\ } \triangleright\!-\!CH_3 \ + \ CH_3CH_2CH=CH_2$$
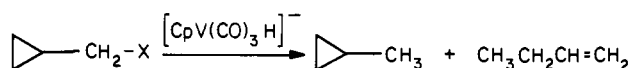
11a, X = Br

11b, X = I

11c, X = OTs

ates with **11b,** giving almost exclusively 1-butene, but an alkylation-reductive elimination process operates nearly exclusively with **11c,** giving methylcyclopropane. In the bromide case (owing to the unusually high two-electron displacement reactivity of the cyclopropylcarbinyl center[20]), the two paths are competitive, giving methylcyclopropane by alkylation-reductive elimination and 1-butene by the radical chain mechanism.[21]

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(1) Only a few other vanadium hydrides are known. See, for example, (a) A. Davison and D. L. Reger, *J. Organomet. Chem.*, **23**, 491 (1970); (b) T. Kruck and H.-U. Hempel, *Angew. Chem., Int. Ed. Engl.*, **13**, 201 (1974); (c) J. E. Ellis and R. A. Faltynek, *J. Organomet. Chem.*, **93**, 205 (1975); (d) J. E. Ellis, R. A. Faltynek, and S. G. Hentges, *J. Am. Chem. Soc.*, **99**, 626 (1977).
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in THF-d₈, the octane product contains *no* deuterium. For data on the optical rotations of optically active deuterated ethylbenzene, see (a) A. Streit-wiesser, J. R. Wolfe, and W. D. Schaeffer, *Tetrahedron Lett.*, 338 (1959); (b) H. J. Dauben and L. L. McKoy, *J. Am. Chem. Soc.*, **81**, 5404 (1959).
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(9) The rate constant for cyclization of this radical (**4b**) has not been measured directly. However, Beckwith and his co-workers have shown that replacement of oxygen for C-3 in a number of substituted 6-hexenyl radicals consistently increases the rate of cyclization by at least an order of magnitude.[10a,b] We have carried out the reduction of **3a** with tri-n-butyltin hydride; using the known value[10c] for the tin hydride chain transfer rate constant (1 × 10⁶ s⁻¹ for primary radicals), we estimate that the rate constant for cyclization **4b** is ~1.0 × 10⁶ s⁻¹.
(10) (a) See, for example, (a) A. L. J. Beckwith, I. Blair, and G. Phillipou, *J. Am. Chem. Soc.*, **96**, 1613 (1974); (b) A. L. J. Beckwith and W. B. Gara, *J. Chem. Soc., Perkin Trans. 2*, 796 (1975); (c) D. J. Carlsson and K. U. Ingold, *J. Am. Chem. Soc.*, **90**, 7047 (1968).
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(15) In the NMR, this material exhibited a single η⁵-C₅H₅ resonance at δ 4.80 ppm.
(16) W. D. Jones and R. G. Bergman, unpublished results.
(17) Control experiments demonstrated that the phosphine complex observed in the photolysis is *not* a result of either thermal or photochemical displacement of Br⁻ from **2**. However, this substitution reaction does occur at a somewhat slower rate, and is responsible for the CpV(CO)₃PPh₃ isolated in preparative-scale reduction experiments.
(18) [(η⁵-C₅H₅)V(CO)₃Br]⁻ also reacts with PPN⁺-1 present in solution to produce another complex, tentatively identified as a hydride-bridged vanadium dimer. Further properties of this material will be reported at a later date (W. D. Jones, R. J. Kinney, and R. G. Bergman, unpublished results).
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(22) National Science Foundation Predoctoral Fellow, 1971–1972; 1975–1977.

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Stereochemistry of 1,4-Conjugate Elimination Reactions

Sir:

In sharp contrast to the intensive studies of the stereochemical course of 1,2-elimination,[1] little is known of the stereochemistry of 1,4-conjugate elimination of allylic leaving groups. Theory predicts that concerted 1,4-conjugate eliminations which produce cisoid dienes should proceed syn,[2] but experimental evidence is sparse and conflicting. The 1,4-elimination component of benzene tetrachloride dehydrochlorination was deduced to be primarily anti,[3] though this conclusion was later disputed.[4] In the most convincing examples provided to date, Cristol et al. showed[5] that syn elimination heavily predominates in the base-catalyzed and thermal eliminations of the 9,10-dihydroanthracenes **1** and related compounds, but the conclusion was later reached that the base-catalyzed eliminations were nonconcerted, proceeding through an E1cB mechanism.[6] An enzyme-mediated example, the chorismate synthetase reaction (eq 1), has been proven to involve stereospecific anti 1,4-elimination.[7]
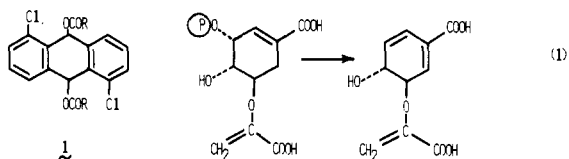
The barrier to providing an unambiguous answer has been largely the difficulty of synthesizing a suitable substrate with isotopically differentiated hydrogens located, in known configuration relative to the leaving group, four carbons distant. We report here the use of stereospecific thermal electrocyclic reactions to prepare stereospecifically 4-deuterated cyclohexenols, which have then allowed elucidation of the stereochemical course of acid-catalyzed, base-catalyzed, and thermal 1,4-eliminations.
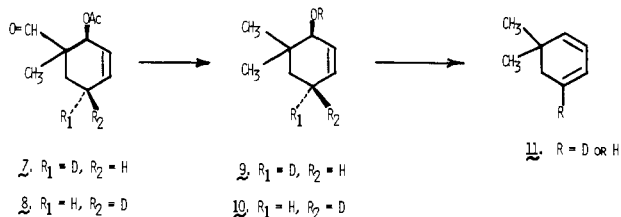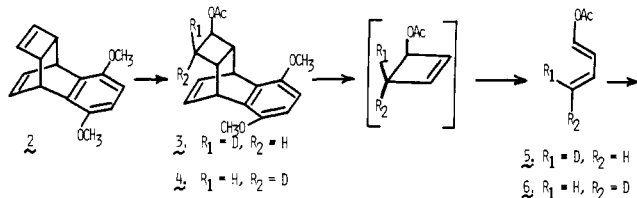
Hydroboration of diene 2^8 with B_2D_6, followed by oxidative workup and acetylation, gave acetate 3, with deuterium cis to acetoxy. Its epimer 4 was prepared by MCPA epoxidation of 2 followed by $LiAlD_4$ reduction and acetylation. Pyrolysis of 3 and 4 at 320-340 °C in a Vycor column packed with glass helices gave the 4-deuterio-1-acetoxybutadienes 5 and 6 respectively in 75-90% yields, along with 1,4-dimethoxynaphthalene. The pyrolysis is pictured as involving retrodiene reversion to 4-deuterio-3-acetoxycyclobutene[9] followed by conrotatory ring opening to 1-acetoxybutadiene. The NMR spectra of 5 ($J_{3,4}$ = 11 Hz) and 6 ($J_{3,4}$ = 17 Hz) confirmed their configurations and geometrical homogeneity.
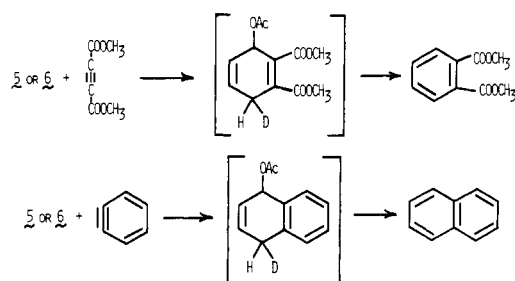
Diels-Alder addition of 5 and 6 to methacrolein gave adducts 7 and 8 converted by Wolff-Kishner reduction to alcohols 9 and 10 (R = H), respectively. These allylic alcohols, prevented by the *gem*-dimethyl substitution from undergoing 1,2-eliminations, and (due to the specificity of the Diels-Alder reaction[10]) containing deuterium at C-4 either trans (9) or cis (10) to the hydroxyl, fit perfectly the substrate requirements cited above.

Dehydration of alcohol 9 (R = H) with *p*-toluenesulfonic acid in xylene at 80 °C gave 5,5-dimethyl-1,3-cyclohexadiene[11] (11) containing 63 ± 3% deuterium by NMR analysis; similar dehydration of 10 (R = H) gave 11 containing 67 ± 2% deuterium. Dehydration of 9 and 10 (R = H) with (carbethoxysulfamoyl)triethylammonium hydroxide inner salt (Burgess' reagent[12]) in *m*-xylene at 25 °C gave 9 containing 47-49% deuterium from either starting material. Not surprisingly, nonstereospecific 1,4-elimination is the result of these two procedures exemplifying acid-catalyzed or solvolytic eliminations via allylic carbonium ions, though the acid-catalyzed reaction shows a clear deuterium isotope effect.

Because stable sulfonate esters of 9 and 10 could not be prepared, the 2,6-dichlorobenzoates[13] were selected for

base-catalyzed eliminations. Elimination with potassium *tert*-butoxide in xylene-Me_2SO mixtures was complicated by deuterium exchange in the products, but this problem was avoided by replacing Me_2SO with 18-crown-6 ether to complex the potassium ion, permitting the elimination to be carried out in a nonpolar medium.[14] Under these conditions (KOBu, *m*-xylene, crown ether, 100 °C), 9 and 10 (R = 2,6-dichlorobenzoyl) afforded 11 containing 90 ± 2 and 15 ± 5% deuterium, respectively. This base-catalyzed 1,4-elimination is consequently predominantly syn.

The stereochemistry of thermal 1,4-conjugate eliminations was examined on 1,4-dihydrobenzenes generated in situ by Diels-Alder addition of 5 and 6 to reactive acetylenic dieno-

philes. We have shown earlier[15] that heating 1-acetoxybutadiene with dimethylacetylene dicarboxylate at 120 °C affords dimethyl phthalate, and that generating benzyne from anthranilic acid in the presence of 1-acetoxybutadiene at 60 °C leads to naphthalene; the Diels-Alder adducts initially formed aromatize by loss of acetic acid (1,4-elimination) under the reaction conditions. When 5 was used in these two reactions, both the dimethyl phthalate and naphthalene formed contained 98 ± 2% deuterium, while the use of 6 led to dimethyl phthalate and naphthalene containing 2 ± 2% deuterium. These thermal 1,4-eliminations are surprisingly stereospecific and almost exclusively syn. Although this stereochemical result would be the consequence of an initial suprafacial 3,3-sigmatropic rearrangement of the allylic ester followed by syn 1,2-elimination, the relatively low temperatures used make the sigmatropic rearrangement unlikely, and the elimination is believed to occur in a single concerted step.

The results reported here represent the first stereochemically unambiguous examples of 1,4-conjugate elimination in simple cyclohexenyl systems. In the thermal eliminations examined, the almost total stereospecificity in each set of isomeric substrates rules out any controlling influence of kinetic isotope effects and reveals syn stereochemistry as an intrinsic property of concerted 1,4-eliminations. The base-promoted elimination is not as cleanly stereospecific and it is possible that two or more mechanisms are competing, though the major one clearly involves syn elimination. Although the experimental conditions employed might be expected to favor a concerted E2 process, it is not possible to rule out a nonconcerted but nevertheless stereospecific E1cB elimination, as found by Cristol in the dihydroanthracene series.[6]

References and Notes

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Electrode Surface Modification
via Polymer Adsorption

Sir:

We are interested in synthesizing electrode surfaces with useful chemical properties. The approach is to chemically bind organic or organometallic compounds to the surfaces of conductors and use these "chemically modified electrodes" to achieve greater specificity in electrode reactions. Recent studies have shown that modifiers, e.g., amines, can be chemically bound to carbon electrodes via the surface oxides.[1-5] Metal oxides, e.g., tin oxide, have been modified by silylation.[6-13] In each case rather stable binding of both electroactive and electroinactive modifiers has been achieved and new chemical properties have been imparted to the electrode. Related studies have shown that electroactive, organic compounds can be strongly adsorbed on platinum[14] and carbon electrodes.[15]

We report here a new approach involving adsorbed polymers. Many polymers strongly adsorb to solids and it appeared that films of one or a few molecular layers could be produced[16] and used independently. The initial experiments reveal the following results. (1) Adsorbed layers of varying thickness can be reproducibly formed using several polymers. (2) Analysis by electron spectroscopy demonstrates that in vacuo the surface is quite uniformly covered and allows an estimate of the layer thickness. (3) These modified surfaces are quite stable and are not destroyed when used in a variety of electrochemical experiments. (4) The polymer layer inhibits electrochemical reactions, but it is shown that reactions can be performed at usual potentials at a surface whose composition is dominated by polymer. (5) An appropriate adsorbed polymer layer can be chemically modified, providing an electroactive surface functionality.

The coating was achieved by dipping platinum wire or sheet into a trifluoroacetic acid solution containing small amounts of ethylene glycol terephthalate polymer (**1**) or a copolymer of 60% lysine, 40% alanine (**2**).[17] After a few minutes the electrode was removed, quickly shaken to remove excess solution and dried in air at 120 °C for 20 min.

Samples coated with **1** (from a 0.03% solution for 7.5 min) were analyzed by scanning Auger electron spectroscopy (AES), providing an elemental analysis of the surface.[18] The spectra showed no fluorine (from trifluoroacetic acid or de-

rivatives), strong carbon and oxygen bands, and markedly attenuated platinum bands. Of the many platinum bands those at 43 and 64 eV and at 1967 eV are of particular interest here. In the spectrum of pure platinum the former pair are some 10 times as intense as the latter. The spectra of the coated samples show the relative intensity of these two pairs to be inverted in comparison with pure platinum. Indeed, the low energy bands are barely detectable. This arises because the electrons ejected at 43 and 64 eV are of relatively low energy so that they have an escape depth of <10 Å. The more energetic electrons analyzed at 1967 eV will, however, escape through some 30 Å.[19] This directly brackets the film thickness between 10 and 35 Å. Etching this sample with an argon ion beam affirms this conclusion. Finally, scanning the sample shows the film to be relatively uniform at the modest resolution of the spectrometer (3-μ electron beam diameter).

There is a correlation between the intensity of the high energy Pt lines and the concentration of the dipping solution. This will be thoroughly explored in a future publication but we note here that AES on the film resulting from a 0.3% solution of **1** showed no high energy platinum lines.

Similar data were obtained using polypeptide **2**. Adsorption from a 0.10% solution of **2** in trifluoroacetic acid, for example, gave a spectrum with no F band, no low energy Pt bands, somewhat depressed high energy Pt lines, and C, N, and O bands of approximately the appropriate intensity considering the polymer structure.

It is of great interest to probe the uniformity of the film. We first note that, although the AES data are averaged over the surface, they are incompatible with a surface thickly covered in some places and uncovered in others. The low energy Pt AES lines are instructive in this regard since they are inhibited by <10 Å of a surface contaminant. If it is assumed that this signal is inversely proportional to the coverage, one concludes that the surface is 99% covered for an electrode prepared from a 0.1% solution of **2** or 0.03% solution of **1**. The question of "narrow, deep holes" is not solved by this approach and, for example, on the 10Å level there must certainly be such defects. Defects were also sought using a Coates and Welter field emission scanning electron microscope. This secondary imaging instrument is capable of 50-Å resolution. Clean platinum showed a very smooth surface marred only by widely scattered, spheroidal screw defects of up to 4000-Å diameter. Platinum/polyester (from 0.15% solution) and platinum/polyamide (from 0.10% solution) were investigated. The polymer coated surfaces were identical with that of clean platinum. To check this a 70-Å layer of gold was vapor deposited on the polymers before the analysis and, again, the surface appeared as defect free as clean platinum. Irregularities were carefully sought by scanning the surface of the screw dislocations but none could be found. It is concluded that, in vacuo, holes and protrusions of polymer are smaller than the resolution of the instruments.

Platinum sheet/polypeptide electrodes prepared identically with those examined spectroscopically were used for electrochemistry. Cyclic voltammetry experiments were performed using dimethyl sulfoxide, 0.1 M tetraethylammonium perchlorate as solvent, and electrolyte. The reduction of 1 mM *n*-propyl-3,5-dinitrobenzamide was investigated. As expected this compound gave a pair of reversible couples on clean platinum, $E_{1/2} = -0.76$ V, -1.14 V. The anodic cathodic peak separation was 75 mV. Using platinum/polypeptide a pair of quasi-reversible couples was again seen $E_{1/2} = -0.76, -1.14$ V. Electrodes prepared from dilute, e.g., 0.03%, solutions gave nearly reversible behavior at slow (100 mV/s) sweep rates. At faster sweep rates the peaks broadened consistent with an inhibited electrochemical rate. This behavior has been quantified and will be reported separately. We emphasize here only that electrodes with considerable amounts of polymer on the surface