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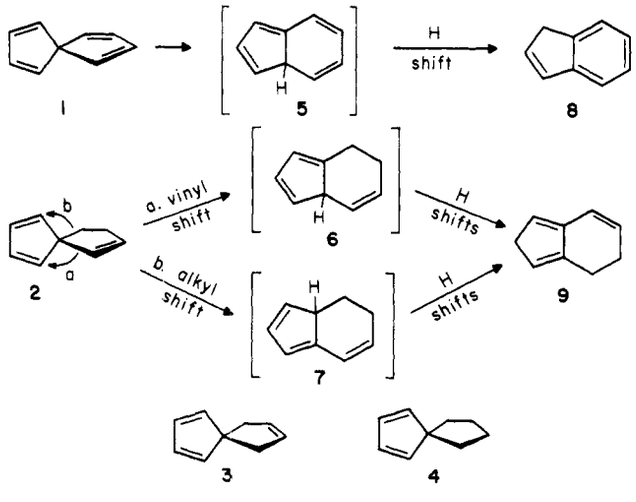
Rapid Vinyl Shifts in Spiro[4.4]polyenes: Verification of the Rate-Determining Step and the Identity of the Migrating Group.

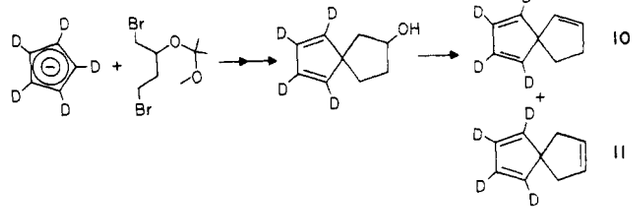
Summary: Pyrolysis studies of 1,2,3,4-tetradeuteriospiro[4.4]nona-1,3,6-triene (**10**) show that the 1,5-sigmatropic shift proceeds with negligible primary deuterium isotope effect, eliminating a rate-determining H shift in this multistep rearrangement. Pyrolysis of 1,2,3,4-tetramethylspiro[4.4]-nona-1,3,6-triene leads to specific vinyl migration, thereby establishing preferential vinyl as opposed to alkyl migration. The structure of the pyrolysis product was determined by an X-ray diffraction structure determination on a crystalline adduct with dimethyl 3,6-dicarboxy-1,2,4,5-tetraazabenzene; the adduct is the result of an unprecedented reaction of the tetrazine.

Sir: Migratory aptitudes in 1,5-sigmatropic shifts are presently not well understood. Examples suggest that sp^2-hybridized carbon migrates at an especially high rate compared to similar saturated carbon substituents.[1-3] This is particularly dramatic in rearrangements of 1,1-disubstituted cyclopentadiene derivatives.[1,2] We were first attracted to the question after observing high rates of unimolecular rearrangement for spiro[4.4]nonatetraene (**1**) and spiro[4.4]nona-1,3,6-triene (**2**) compared to spiro[4.4]nona-1,3,7-triene (**3**) and spiro[4.4]-nona-1,3-diene (**4**).[2] Using a picture in which the transition state for carbon shift in compounds **1-4** resembles a carbon unit migrating around a cyclopentadienyl radical, we[2] and others[1] have proposed that the rate enhancement ($\sim 10^4$ for **1**, 10^3 for **2**) is due to π^* (LUMO) of a migrating vinyl substituent interacting with the HOMO for the cyclopentadienyl unit.



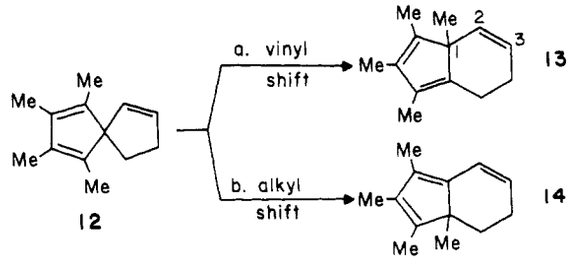
Experimental support of this mechanism has been lacking, however, due to the fact that the expected first products (**5**, **6**) from rearrangement of **1** and **2** have not been observed or trapped; presumably, they rearrange rapidly via 1,5-hydrogen shifts to the more stable (observed) isomers, **8** and **9**. This allows at least two alternate explanations for the high reactivity of **1** and **2**. First, it might be that the carbon shift (**1** → **5** and **2** → **6**) is fast and reversible and then the hydrogen shift is rate determining.[4] Second, it might be that the presence of a vinyl group facilitates the migration of the geminal substituent (vinyl for **1**, alkyl for **2**). With **2**, a vinyl shift would give **6** and a "vinyl-assisted" alkyl shift would give **7**; both products could reasonably produce the observed product, **9**, via hydrogen shifts. In the present work, we have focused on rearrangement of **2** and established that: (1) the hydrogen shift is *not* rate determining; and (2) the vinyl substituent *is* the migrating group.

Since deuterium isotope effects for 1,5-hydrogen shifts in substituted cyclopentadienes fall in the range k_H/k_D = 4.5-7.7,[5] a rate-determining hydrogen shift in the rearrangement of **2** would mean a substantially slower rate of rearrangement for the deuterium-labeled analogue **10**. Our synthesis[2] of **2** is not readily amenable to the preparation of **10**, so we developed a new approach via the reaction[7] of the cyclopentadienyl anion (perdeuterio[8]) with 1,4-dibromo-2-(1-methyl-1-methoxyethoxy)butane.[9] The initial adduct was converted (a. thionyl chloride; b. potassium *tert*-butoxide) to a mixture of 1,2,3,4-tetradeuteriospiro[4.4]nonatriene isomers **10** and **11** (92-93% deuterium incorporation by ^{1}H NMR analysis). The isomers were separated by GLC and



subjected to gas-phase pyrolysis, as described before.[2] The isomers **2** and **3** were pyrolyzed in a precisely parallel way. Comparing rearrangement of **2** and **10** at 95.7 °C showed k_H/k_D = 1.0 ± 0.1 (average of five runs). Comparing rearrangement of **3** and **11** at 158.2 °C showed k_H/k_D = 1.1 ± 0.2 (average of three runs). Therefore, the rate-determining step for rearrangement of **2** and **3** is not the hydrogen shift.

To support the idea that the vinyl group in **2** is migrating preferentially, we studied reactions of 1,2,3,4-tetramethylspiro[4.4]nona-1,3,6-triene (**12**). This analogue of **2**, prepared according to the method of Criegee,[10] can undergo either vinyl migration (to give **13**) or alkyl migration (to give **14**); isomerization via 1,5-hydrogen shift is not available, and the corresponding 1,5-methyl shift (in **13** or **14**) is expected to have a substantially higher activation barrier, perhaps 45 kcal/mol.[11]



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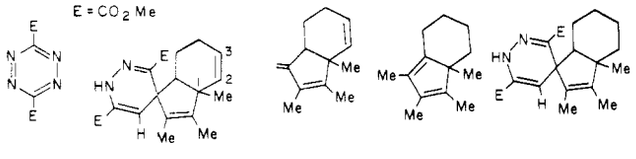
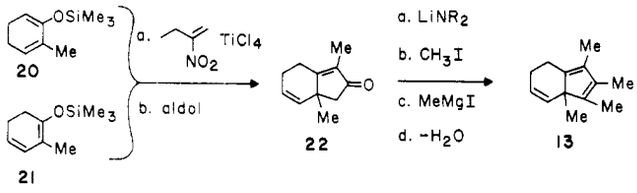
Preparative-scale flow pyrolysis[2] of **12** at 345 °C (0.04 Torr) led to partial conversion to a single product, X; more complex mixtures were obtained at higher temperatures. Product X was isolated by preparative GLC and found to show ^{1}H NMR, IR, and mass spectral data[12] consistent with either structure **13** or **14.** In order to define the structure of X, a crystalline adduct (mp 166–166.5 °C) was prepared by reaction (25 °C, 12 h, dichloromethane solution) with 3,6-dicarbomethoxytetrazine (**15**). Our expectation that the adduct arose via Diels–Alder reaction, with **15** as the diene component, followed by loss of dinitrogen[13] was supported by the elemental composition ($C_{19}H_{24}N_2O_4$), but was clearly inconsistent with the ^{1}H NMR spectrum of the adduct.[14] Therefore an X-ray diffraction study was undertaken.

Crystals formed in the triclinic space group $P\bar{1}$ with a = 8.085 (3), b = 10.326 (4), and c = 12.207 (5) Å, α = 109.83 (1), β = 88.53 (1), and δ = 109.70 (1)°, and one molecule of $C_{19}H_{24}O_4$ in the asymmetric unit. A total of 2379 unique intensity data ($2\theta \leq 114°$, Cu K_α radiation) were measured and 1530 (64%) were judged observed after correction for Lorentz, polarization, and background effects. Solution via a weighted, multiple solution sign determining procedure[15] and refinement[16] were uneventful. The final crystallographic residual is 0.095 for the observed reflections and metric details agree well with generally accepted values.[17] The structure of the adduct is **16.**



While **16** is formally the [4 + 2] adduct (loss of dinitrogen) of tetrazine **15** with the *exo*-methylene isomer (**17**), the actual mechanim of the formation of **16** is not clear. It is clear that the structural relationship between the isolated double bond (C_2–C_3) and the quaternary methyl group (at C_1) is the same in **13** and **16.** There remains the possibility, however, that the isolated double bond started out as in **14** and migrated to the observed position in **16** during reaction with the tetrazine. The fact that the saturated analogue[18] **18** reacts with tetrazine **15** in a precisely parallel way (to give **19**)[20] shows that the isolated double bond in **13** is not necessarily involved in this type of reaction.

Further evidence for the structure of X was provided by rational synthesis. Reaction of 2-methylcyclohex-2-en-1-one with chlorotrimethylsilane and triethylamine in dimethylformamide at reflux led to a mixture of sensitive products, tentatively characterized as enol ethers **20** and **21.** Reaction



of this mixture with 2-nitro-1-butene according to the method of Yoshikoshi,[19] followed by aldol condensation, led to a single distillable product (**22**) in low overall yield.[20] Methylation of the kinetic enolate anion of **22,** followed by addition of methylmagnesium bromide and spontaneous elimination of water, afforded a hydrocarbon identical[21] with the pyrolysis product (X = **13**).

We conclude that 1,5-vinyl shifts are favored over 1,5-alkyl migrations in the spirocycles, and that subsequent hydrogen shifts are not rate determining. It is now appropriate to focus on the central question: Why does the vinyl group migrate easily?[22]

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(12) ^{1}H NMR (90 MHz, CCl_4) δ 5.30–5.75 (m, 2 H), 2.00–2.80 (m, 4 H), 1.75 (s, 9 H), 0.95 (s, 3 H); IR 3010 (w), 2940 (m), 2900 (s), 2850 (m), 1630 (w); mass spectrum *m/e* 174.
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(14) The product had mp 166–166.5 °C; ^{1}H NMR (90 MHz, $CDCl_3$) δ 8.00 (s, 1 H), 5.50–5.70 (m, 3 H), 3.80 (s, 3 H), 3.75 (s, 3 H), 2.25–2.45 (m, 2 H), 1.80–2.10 (m, 3 H), 1.67 (s, 3 H), 1.57 (s, 3 H), 1.14 (s, 3 H); IR 3450 (m), 3000 (w), 2980 (w), 2950 (m), 2900 (w), 1720 (s); UV (EtOH); λ_{max} 270 (ϵ 8400), 357 nm (ϵ 2800); mass spectrum *m/e* 344.1753, calcd for $C_{19}H_{24}N_2O_4$, 344.1734.
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(17) Full experimental details can be found in ref 7.
(18) Compound **18** was prepared according to the general scheme shown for preparation of **13** (**20** + **21** → **22** → **13**) starting from 2-methyl-1-(trimethylsilyloxy)-1-cyclohexene; the general method and the specific first steps are reported.[19]
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(20) Compounds **13, 16, 18, 19,** and **22** showed ^{1}H NMR, IR, UV, and mass spectral data consistent with the proposed structures. Crystalline derivatives were prepared which gave either satisfactory microanalyses or exact mass spectra.
(21) Compound **13** prepared from **22** showed ^{1}H NMR and IR spectral data and GLC retention time identical with parallel measurements for **13** obtained from pyrolysis, and reacted with **15** to give **16.**
(22) We are pleased to acknowledge support from the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.
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Homologation–Alkylation of Carbonyl Compounds via Regiospecifically Generated Metallo Enamines

Summary: A novel and efficient synthetic strategy for effecting the geminal substitution at a carbonyl center has been

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