

and that the Fe-carbon bonds in **3** average 37 kcal/mol or more, then the condition will be met and the overall process forming **3** will be exothermic. The Fe-carbon bonds in **3** certainly average at least 37 kcal/mol. Hence the proposed structures are reasonable from a thermodynamic viewpoint.

It has been reported that $D(\text{Cr}^+-\text{C}_6\text{H}_6) \approx 50$ kcal/mol.¹⁵ If this is indicative of the strength of the Fe^+ -arene interaction in **2** and the analogous triphenylene complex, then formation of those structures as products of the observed reactions would also be exothermic.

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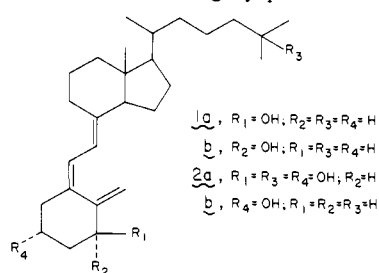
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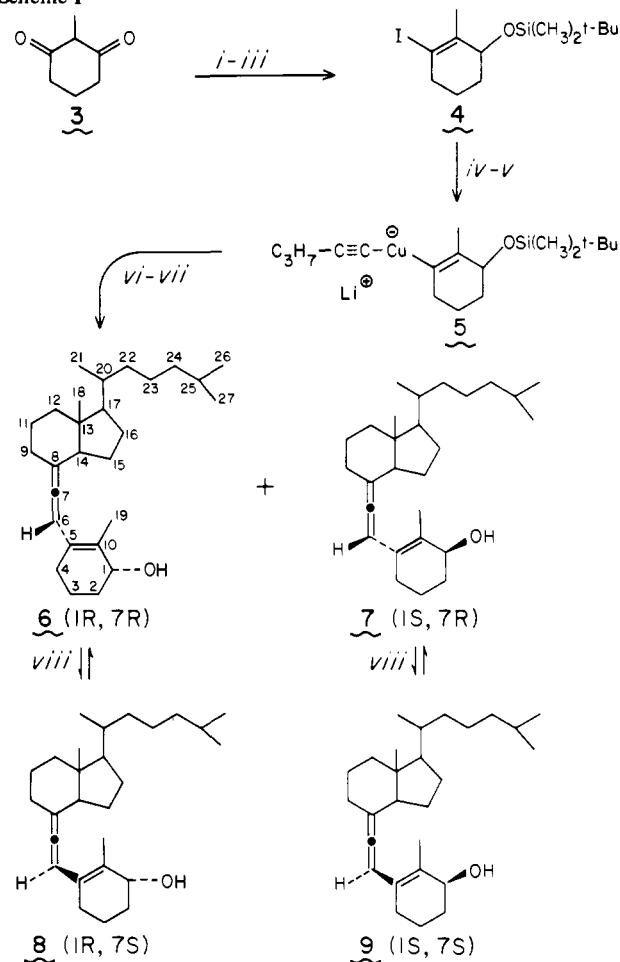
Sigmatropic Rearrangement of Vinylallenes: A Novel Route to the 1-Hydroxyvitamin D System¹

Sir:

We wish to describe our initial results on the preparation and sigmatropic rearrangement of vinylallene intermediates for synthesizing the physiologically important 1-hydroxyvitamin D system.²⁻⁴ As the first example of this approach, we describe a synthesis of 3-deoxy-1-hydroxyvitamin D₃, whose 1 α or 1S epimer⁵ **1a** is known to be a highly potent analogue of the



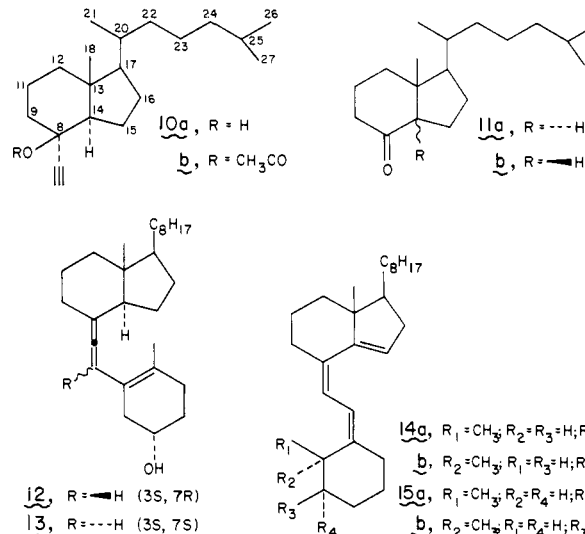
Scheme I



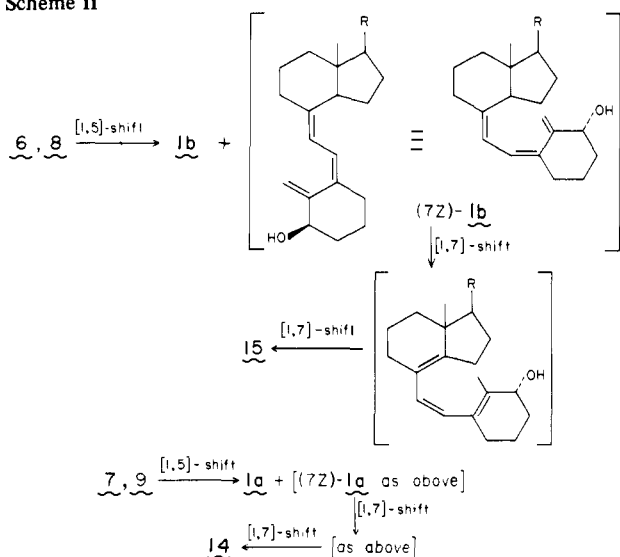
Reagents: *i*, Ph_3PI_2 , Et_3N , CH_3CN , reflux 3 hrs. (76%); *ii*, NaBH_4 , EtOH , RT, 3 hrs. (88%); *iii*, $t\text{-Bu}(\text{CH}_3)_2\text{SiCl}$, imidazole, DMF, RT, 3 hrs. (97%); *iv*, $t\text{-BuLi}$, -78° (2 hrs.), -30° (1 hr.); *v*, $\text{C}_3\text{H}_7\text{C}\equiv\text{C}-\text{Cu}\cdot 2\text{P}(\text{N}(\text{CH}_3)_2)_3$, -78° , 1 hr.; *vi*, $\underline{10b}$, -78° , 5 hrs.; *vii*, $\text{Bu}_4\text{N}^+\text{F}^-$, THF, RT, 4 hrs. (37% based on $\underline{10b}$); *viii*, hv, hexane, RT, 1 hr. (33%).

naturally occurring steroid hormone 1 α ,25-dihydroxyvitamin D₃ (**2a**).⁶

Scheme I summarizes the synthesis of the vinylallenes where the key step is the coupling of cuprate **5** with the ethynyl acetate **10b**.⁷ The latter was prepared from Grundmann's ketone **11a**⁸ (**2b**, $\text{O}_3/\text{CH}_3\text{CH}_2\text{CHO}$, 75-92%)⁹ by treatment with



Scheme II



$\text{LiC}\equiv\text{CH}$ (THF, -78°C , 90%)¹⁰ and then Ac_2O ($\text{C}_5\text{H}_5\text{N}$, Δ , 36 h, 88%).^{11,12} The coupling⁷ of **5**¹³ and **10b** followed by deprotection^{14b} afforded a 37% yield of a mixture of **6** and **7**,¹⁴ which was chromatographed to give pure **6** (10%, less polar) and **7** (12%, more polar).^{11,14} Photolysis of **6** produced a 1:1 mixture of **6** and **8**; similarly **7** gave a 1:1 ratio of **7** and **9**.¹⁵ These $Z \rightleftharpoons E$ photoisomerizations proceed analogously to that observed for the known vinylallenes **12** and **13**.³ Because **7**, **9** and **6**, **8** are convertible to **1a**⁵ and **1b**, respectively (below), they are assigned the 1S and 1R configurations, respectively. The allene configurations are tentatively assigned on the basis of spectral comparisons (¹H NMR, C-18 methyl) with **12** and **13**.³ The C-18 methyl resonance of **6** or **7** (τ 9.34 for both) is similar to that of the 7R isomer **12** (τ 9.35); for **8**, **9**, and 7S isomer **13**, this same resonance appears at τ 9.29, 9.28, and 9.27, respectively. Thus, the coupling of vinyl cuprate **5** with **10b**, a formal $\text{S}_{\text{N}}2'$ process, occurs in a completely anti fashion. Certain dialkyl cuprate additions are known to exhibit similar anti selectivity,^{7b} but exceptions are known.⁷

The allene **6** on thermolysis (refluxing isooctane, 8 h, N_2) afforded a $\sim 52\%$ yield of **1b** as well as $\sim 5\%$ C and $\sim 4\%$ D. By contrast the C_1 epimer, **7**, gave only $\sim 11\%$ of the corresponding vitamin **1a**⁵ accompanied by major amounts of A ($\sim 41\%$) and B ($\sim 23\%$).¹¹ There was essentially a reversal of product proportions when the photoisomers **8** and **9** were heated: **8** gave only $\sim 9\%$ **1b**, but $\sim 45\%$ C and $\sim 18\%$ D; **9** produced $\sim 31\%$ **1a**, $\sim 4\%$ A, and $\sim 5\%$ B.^{11,14}

The four stereoisomers A–D possess similar spectral properties (UV, ¹H NMR) and are tentatively assigned as **14a**, **14b**, **15b**, and **15a**, respectively. The assigned intericyclic diene stereochemistry rests on the rational mechanistic pathway proposed in Scheme II. The major isomer (A or **14a** and C or **15b**) in each case from heating **7** and **8**, respectively, exhibited ~ 7 -Hz bandwidths due to the C_1 proton in the NMR, while the minor isomers (B or **14b** and D or **15a**, respectively) exhibited larger bandwidths of ~ 23 Hz. The smaller bandwidth implies that the hydroxyl at C_1 and methyl at C_{10} are trans diaxially related in **14a** and **15b**; the larger bandwidth (due to trans- $\text{C}_{1,2}$ -proton coupling) indicates that methyl and OH are cis in **14b** and **15a** with the methyl group fixed axially.¹⁶ Since the C_1 configuration is presumably unchanged during the thermolysis, the C_{10} configurational assignment follows.¹⁷

Our original synthesis of **1a** from cholesterol required 11 steps (0.2% overall yield).⁵ The present convergent synthesis of **1a** involves 6–7 steps (0.7% overall yield from readily available vitamin D_3); the epimer **1b** requires 6 steps (3% overall). The new vinylallene scheme, which will likely improve

on further exploratory studies, is made especially attractive by the fact that a host of A-ring fragments should be obtainable from the commonly available 2-methyl-1,3-cycloalkanediones.

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Supplementary Material Available: Spectral and analytical data (7 pages). Ordering information is given on any current masthead page.

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- (14) The crude product consists of a relatively simple mixture of the desired vinylallenes, **10b**, and protonated **5** (by NMR). Prolonged reaction times or higher temperatures did not improve the yield of vinylallene. Two to three cycles of silica gel chromatography (67×1.5 cm column, 10–15% ether in 30–60 $^\circ\text{C}$ low boiling petroleum ether) effected separation of pure (TLC, NMR) **6** and **7** and the various isomeric **14**–**15** trienes. The isomers **6**–**9** and **14**–**15** exhibited no exceptional instability over many months (in ether under nitrogen, freezer).
- (15) Hanovia 100-W mercury arc, quartz, 5×10^{-3} M (hexane), N_2 ; purification according to note 14 (yield, 1:1 mixture, quantitative).
- (16) For the analogous 10,19-dihydrovitamins derived from vitamin D_3 (W. H. Okamura, M. L. Hammond, A. Rego, A. W. Norman, and R. M. Wing, *J. Org. Chem.*, **42**, 2284 (1977)), the C_{10} methyl is forced into an axial orientation.
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Crossed Molecular Beam Study of the Chemionization Reaction: $\text{SbF}_5 + \text{RX} \rightarrow \text{SbF}_5\text{X}^- + \text{R}^+$

Sir:

We report the title gas-phase chemionization reaction with $\text{RX} =$ benzyl chloride, *tert*-butyl chloride (bromide, iodide), isobutyl iodide, isopropyl iodide, allyl bromide, bromoacetyl