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 $D(\mathrm{Cr}^+\text{-}\mathrm{C_6H_6}) \simeq 50$ 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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(8) A referee properly points out that a structure analogous to **3** but with four phenyl groups would be quite strained even with phenyl group rotation. A metal capable of higher oxidation states might form $\mathrm{M(C_{18}H_{12})_2}^+$.
(9) Determined using the following values of ΔH°_{f298} in kilocalories/mole from H. M. Rosenstock, K. Draxl, B. W. Steiner, and J. T. Herron, *J. Phys. Chem. Ref. Data,* **6,** Suppl. 1 (1977): $\mathrm{Fe}^+ = 280.4$, $\mathrm{C_6H_5Br} = 25.1$, $\mathrm{HBr} = -8.7$, $\mathrm{C_6H_5I} = 38.9$, and $\mathrm{I} = 25.5$
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(16) NSF Undergraduate Research Participant.

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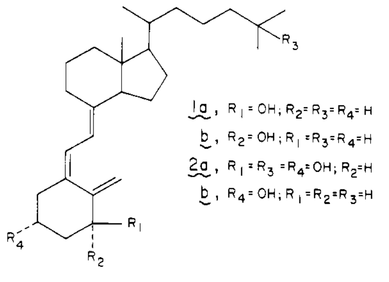
Sigmatropic Rearrangement of Vinylallenes: A Novel Route to the 1-Hydroxyvitamin D System[1]

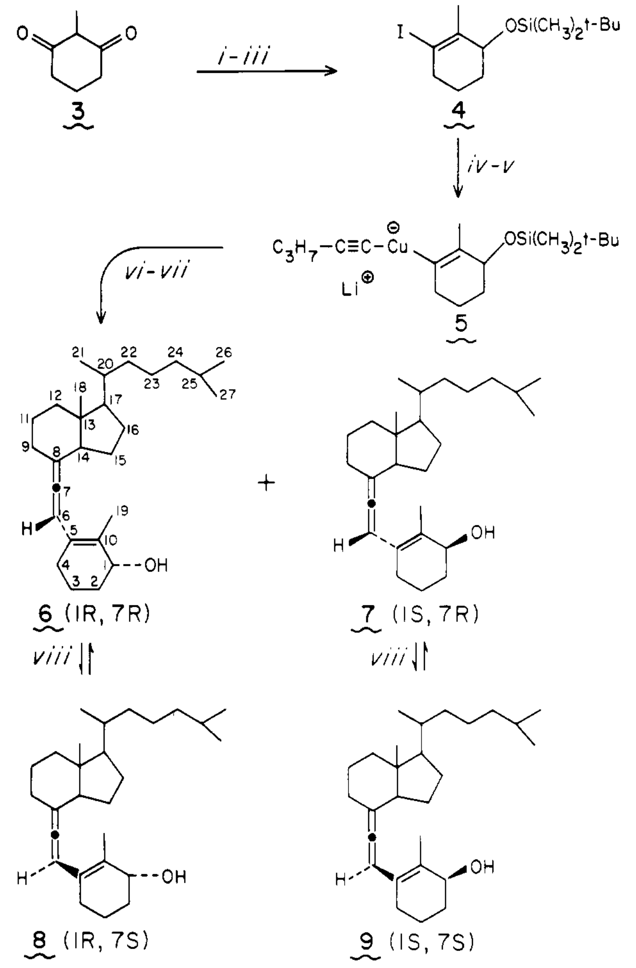
Sir:

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 $\mathrm{D_3}$, whose 1α or 1*S* epimer[5] **1a** is known to be a highly potent analogue of the naturally occurring steroid hormone 1α,25-dihydroxyvitamin $\mathrm{D_3}$ (**2a**).[6]



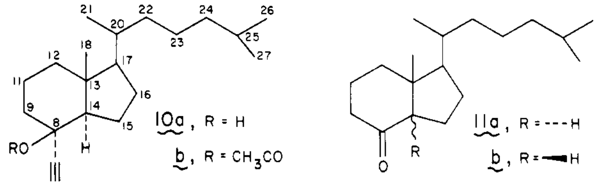
1a, $R_1 = OH; R_2 = R_3 = R_4 = H$
b, $R_2 = OH; R_1 = R_3 = R_4 = H$
2a, $R_1 = R_3 = R_4 = OH; R_2 = H$
b, $R_4 = OH; R_1 = R_2 = R_3 = H$

Scheme I

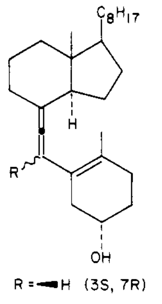


Reagents: *i*, $\mathrm{Ph_3PI_2}$, $\mathrm{Et_3N}$, $\mathrm{CH_3CN}$, reflux 3 hrs. (76%); *ii*, $\mathrm{NaBH_4}$, EtOH, RT, 3 hrs. (88%); *iii*, t-$\mathrm{Bu(CH_3)_2SiCl}$, imidazole, DMF, RT, 3 hrs. (97%); *iv*, t-BuLi, −78° (2 hrs.), −30° (1 hr.); *v*, $\mathrm{C_3H_7C{\equiv}C{-}Cu{\cdot}2P(N(CH_3)_2)_3}$, −78°, 1 hr.; *vi*, **10b**, −78°, 5 hrs.; *vii*, $\mathrm{Bu_4N^+F^-}$, THF, RT, 4 hrs. (37% based on **10b**); *viii*, $h\nu$, hexane, RT, 1 hr. (33%).

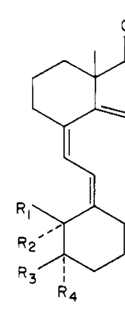
Scheme I summarizes the synthesis of the vinylallenes where the key step is the coupling of cuprate **5** with the ethynyl acetate **10b.**[7] The latter was prepared from Grundmann's ketone **11a**[8] (**2b,** $\mathrm{O_3/CH_3CH_2CHO}$, 75–92%)[9] by treatment with



10a, R = H
b, R = $\mathrm{CH_3CO}$
11a, R = ---H
b, R = ◄H

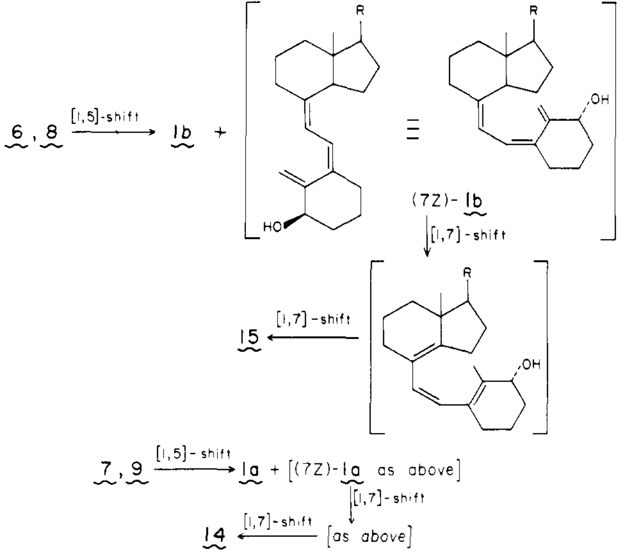


12, R = ◄H (3S, 7R)
13, R = ---H (3S, 7S)



14a, $R_1 = CH_3; R_2 = R_3 = H; R_4 = OH$
b, $R_2 = CH_3; R_1 = R_3 = H; R_4 = OH$
15a, $R_1 = CH_3; R_2 = R_4 = H; R_3 = OH$
b, $R_2 = CH_3; R_1 = R_4 = H; R_3 = OH$

Scheme II



$LiC\equiv CH$ (THF, −78 °C, 90%)[10] and then Ac_2O (C_5H_5N, Δ, 36 h, 88%).[11,12] The coupling[7] 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 $Z \rightleftarrows E$ 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 1*S* and 1*R* configurations, respectively. The allene configurations are tentatively assigned on the basis of spectral comparisons (^{1}H 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 7*R* isomer **12** (τ 9.35); for **8**, **9**, and 7*S* 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 S_N2' 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 ∼52% yield of **1b** as well as ∼5% C and ∼4% D. By contrast the C_1 epimer, **7**, gave only ∼11% of the corresponding vitamin **1a**[5] accompanied by major amounts of A (∼41%) and B (∼23%).[11] There was essentially a reversal of product proportions when the photoisomers **8** and **9** were heated: **8** gave only ∼9% **1b**, but ∼45% C and ∼18% D; **9** produced ∼31% **1a**, ∼4% A, and ∼5% B.[11,14]

The four stereoisomers A–D possess similar spectral properties (UV, ^{1}H NMR) and are tentatively assigned as **14a**, **14b**, **15b**, and **15a**, respectively. The assigned intercyclic 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-$C_{1,2}$-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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(11) Absolute weighed yields are given except for the minor components (4–5%; based on UV calculations) produced on thermolyzing **6** and **9**.

(12) The epimer **11b**[8] affords an apparently homogeneous alcohol different from **10a** and it is probably doubly epimeric to **10a** (C_8 and C_{14}).

(13) (a) E. Piers and I. Nagakura, *Synth. Commun.*, **5**, 193 (1975), and personal communications; (b) E. J. Corey and A. Venkateswarlu, *J. Am. Chem. Soc.*, **94**, 6190 (1972); (c) E. J. Corey and D. J. Beames, *ibid.*, **94**, 7210 (1972).

(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 °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.

(17) See A. Verloop, G. J. B. Corts, and E. Havinga, *Recl. Trav. Chim. Pays-Bas*, **79**, 164 (1960), for possibly analogous rearrangements involving *cis*-isotachysterol.

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Crossed Molecular Beam Study of the Chemionization Reaction: $SbF_5 + RX \rightarrow SbF_5X^- + R^+$

Sir:

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

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