Simpson.[16] Final parameters are available as supplementary material.

Determination of Absolute Configuration. The absolute configuration of the compounds were determined by the Bijvoet method using Br and Cl atoms as anomalous scatterers. Cu Kα and Mo Kα radiations were used for compounds **3** and **5**, respectively. Fifteen pairs of reflections for each compound were selected for this purpose. The selections were made on the basis of the largest values of $(F_+^2 - F_-^2/\sigma(F_o^2)$. Values of F_+^2 and F_-^2 were calculated according to the method of James.[17] Intensities I_{hkl} and $I_{\bar{h}\bar{k}\bar{l}}$ of the Friedel pairs were measured. The results are available as supplementary material. For both compounds all observations agreed, establishing the absolute configuration shown in all figures.

Acknowledgment. We thank Dr. Mike Wilson, Haliburton Services Co. for ^{13}C microanalysis of isodeodactol (**8**). High-resolution mass spectral analyses were provided by the mass spectrometry facility at the Massachusetts Institute of Technology, supported by a grant (prinicpal investigator Professor K. Biemann) from the Biotechnology Research Branch, Division of Research Resources. The 360-MHz NMR spectra were attained at the Purdue Biochemical Magnetic Resonance Laboratory supported by NIH Grant RR 01077. We thank Dr. Paul Schmidt, Oklahoma Medical Research Foundation, Oklahoma City, for use of a Bruker 270-MHz NMR instrument and assistance in its operation. We acknowledge with thanks grants from the NSF (GP 38410) and the Phillips Petroleum Co., which aided in the purchase of NMR spectrometers.

Registry No. **3**, 79433-81-1; **4**, 79433-82-2; **5**, 79373-29-8; **6**, 79433-83-3; **7**, 79373-30-1; **8**, 79373-31-2.

Supplementary Material Available: Final positional parameters, anisotropic thermal parameters, hydrogen atom positional and thermal parameters, bond angles, observed and calculated Bijvoet differences, and torsion angles for **3** and **5** (11 pages). Ordering information is given on any current masthead page.

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Synthesis and Thermolysis of *A*-Norvinylallenes Related to Vitamin D[1]

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Received July 2, 1981

Coupling the lithium salt of allene hydrocarbon **9** with keto enol ether **10** produced a 12:1 diastereomeric mixture of *A*-norvinylallenones **6a** (6*R*) and **6d** (6*S*). The absolute configuration of *A*-norallenes **6a** (6*R*) and **6d** (6*S*) were assigned by comparison of their ^{13}C NMR and ^1H NMR spectra with those of the previously studied six-membered A-ring vinylallenes **4a** (6*R*) and **4d** (6*S*). Thermolysis of **6a** (140 °C, 24 h) afforded **11** (6%), **12** (5%), **13** (35%), and **14** (6%). A similar result was obtained for **6d**: **11** (~5%), **12** (~1%), **13** (39%), and **14** (~3%). Reduction ($NaBH_4$–$CeCl_3$/MeOH) of **6a** yielded vinylallenols **6b** (1*R*,6*R*) and **6c** (1*S*,6*R*). Similar reduction of **6d** gave **6e** (1*R*,6*S*) and **6f** (1*S*,6*S*). Thermolysis of the vinylallenols led to complex, undefinable products. The thermal behavior of *A*-norvinylallenes **6** is discussed in terms of previous results obtained for the six-membered-ring series.

Vinylallenes of the type **1** may undergo competitive thermal [1,5] sigmatropic shifts to afford the *E* (**2**) or *Z* (**3**) trienes[2] (Scheme I). A detailed investigation of the vitamin D type vinylallenes **4a–f** revealed that the *E* to *Z* pathway ratio is sensitive to the functional group at C_1.[2b,d] The desired *E* pathway, which corresponds to the vitamin D–triene system **5**, was observed to be maximal for the diastereomeric alcohols **4b** (1*R*,6*R*) and **4f** (1*S*,6*S*). In stark contrast, the corresponding epimeric alcohols **4c** (1*S*,6*R*) and **4e** (1*R*,6*S*), respectively, rearranged primarily by way of the *Z* pathway to afford the unnatural 7*Z* isomer of **5**. In order to develop a better understanding of this phenomenon, we have initiated studies of structurally modified vinylallenes. In this paper we report on the synthesis and thermal investigation of the corresponding *A*-nor analogues **6a–f**.

A further impetus for carrying out this investigation was the earlier finding that 3-deoxy-1α-hydroxyvitamin D_3 (**5a**), a biologically active analogue of 1α,25-dihydroxyvitamin D_3 (**8a**), exhibited selective biological activity.[3,4] Whereas the natural steroid hormone **8a** is the most active substance known[5] for eliciting both classical vitamin D mediated responses, intestinal calcium absorption (ICA) and bone calcium mobilization (BCM), the analogue **5a** exhibited only ICA, a characteristic of potential clinical

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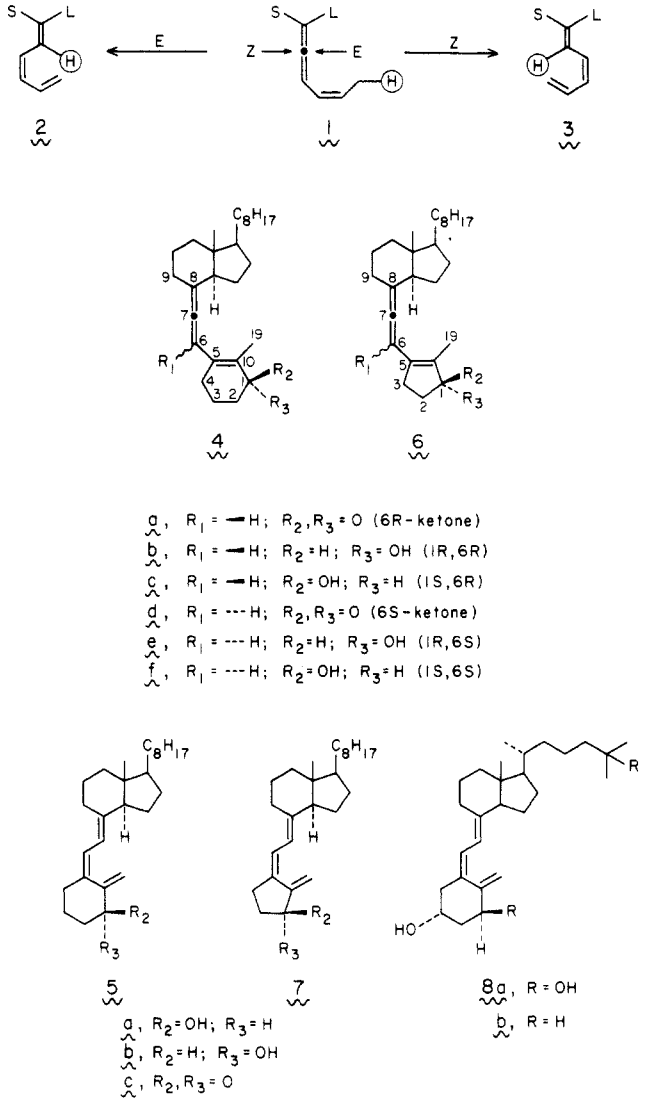
Table I. NMR Data[a] for Allenes 4 and 6

compd	J^b	^{1}H NMR[c]	^{13}C NMR[d]	compd	J^b	^{1}H NMR[c]	^{13}C NMR[d]
6*R* ketone **6a**	2.9	9.32	11.94	**4a**	2.9	9.32	11.97
1*R*,6*R* alcohol **6b**	3.0	9.34	11.96	**4b**	3.1	9.35	11.91
1*S*,6*R* alcohol **6c**	3.0	9.35	11.96	**4c**	3.2	9.35	11.94
6*S* ketone **6d**	3.6	9.26	12.38	**4d**	3.5	9.25	12.45
1*R*,6*S* alcohol **6e**	3.6	9.32	12.28	**4e**	3.6	9.30	12.40
1*S*,6*S* aocohol **6f**	3.6	9.30	12.22	**4f**	3.5	9.30	12.42

[a] Recorded in $CDCl_3$ with $(CH_3)_4Si$ as an internal standard: ^{1}H NMR, Varian EM-390, τ values; ^{13}C NMR, Bruker WH90D-18 multinuclear FT NMR, δ values. [b] ^{1}H NMR, J(Hz), H_6 appears as a triplet due to equivalent splitting by $H_{9\alpha}$ and $H_{14\alpha}$. [c] ^{1}H NMR, τ, C_{18} methyl. [d] ^{13}C NMR, δ, C_{18}.

Scheme I



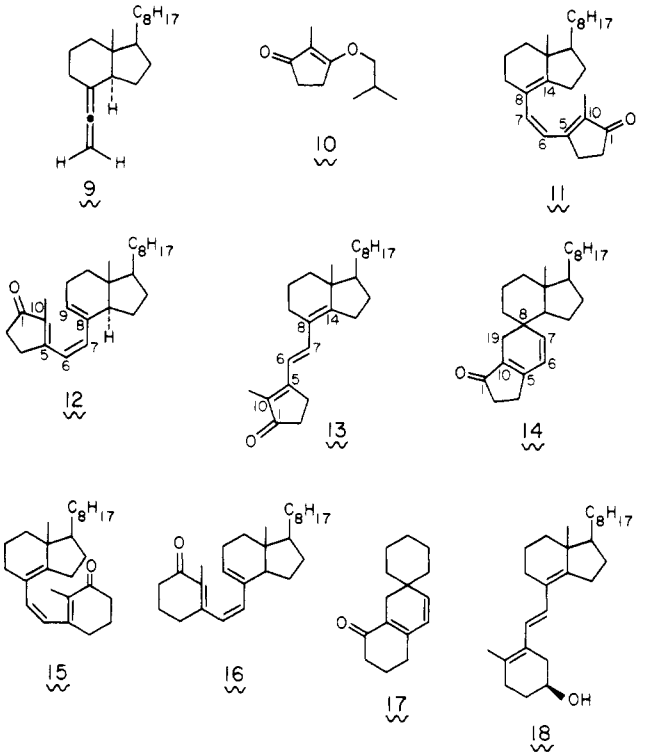
utility. Thus, it was of some interest to direct our attention to the *A*-nor (**7**) and *A*-homo (not shown) analogues of **5a**.

Results and Discussion

The synthesis of the vinylallenes **6a–f** was patterned after the preparation of **4a–f**.[2d] The lithium salt (*tert*-butyllithium, ether, −78 °C) of **9** was reacted with keto enol ether **10** and hydrolytically rearranged to afford a 93% yield of a 12:1 mixture of allenones **6a** and **6d**. Separation by chromatography afforded pure **6a** in 55% yield. Photoisomerization of **6a** afforded a 1:1 mixture of **6a** and **6d**, which after separation gave pure (6*S*)-allene **6d** (77% based on recovered **6a**). Luche reduction[6] ($NaBH_4$, $CeCl_3$, CH_3OH) of **6a** afforded **6b** and **6c** in high yield in a nearly

(6) Luche, J. *J. Am. Chem. Soc.* **1978**, *100*, 2226.

Chart I



1:1 ratio; similar results were obtained for the reduction of **6d** to **6f** and **6e**. Reduction in the absence of $CeCl_3$ resulted in apparent carbon–carbon double bond reduction.

The absolute configuration of the allene group in **6a–f** readily follows from the methods of synthesis. It was shown previously that the lithium salt of **9** (see Chart I) reacts with the six-membered-ring analogue of **10** to produce a remarkably stereoselective 13.5:1 ratio of 6*R* (**4a**) to 6*S* (**4d**) ketones.[2d] Thus, the major isomer resulting from coupling the salt of **9** with **10** is undoubtedly also the 6*R* ketone **6a**. Moreover, comparison of three pieces of NMR data (the magnitude of the coupling constant between H_6 and the α-protons on C_9 and C_{14}, the ^{1}H NMR C_{18} angular methyl group chemical shift, and the ^{13}C NMR C_{18} signal) reveals a complete parallel between the **4a–f** and **6a–f** series. These data are summarized in Table I.

The C_1 configurational assignments for the epimeric pairs of alcohols **6b,c** and **6e,f** follow in part from a comparison of their specific rotations. The more dextrorotatory isomer of each pair ($[\alpha]^{25}_D$ (*c* 1 g/100 mL, $CHCl_3$), Perkin-Elmer Model 241 polarimeter: **6b**, +14° and **6c**, −104°, **6e**, +174° and **6b**, +37°) is assigned the *R* configuration in parallel with the firmly established six-membered-ring series[2b] **4b,c** and **4e,f**. In addition, the chromatographic elution order for the epimeric pairs in the five-membered-ring series parallels that in the six-membered-ring system.[2d] It should be noted, however, that the method based on comparison of specific rotations was

generalized by Mills[7] for cyclohexenols and not cyclopentenols.

The matter of C_1 configurations was not pursued further because the thermal experiments proved unsatisfactory. Whereas the mode of rearrangement in the six-membered-ring series (4) proceeded in a manner ascribable to [1,5] and [1,7] sigmatropic hydrogen shifts[2d] (100 °C, 10–20 h for completion), the five-membered-ring alcohols (**6b,c,e,f**) remained essentially unchanged under similar conditions. When the thermolysis at higher temperatures (120–140 °C) was monitored by UV spectroscopy, absorption in the region >230 nm gradually vanished. Analysis by ^{1}H NMR of a typical product mixture (*n*-decane, 24 h at 140 °C, nitrogen) revealed that absence of significant olefinic resonances. HPLC monitoring (dual UV and refractive index detection) revealed the simultaneous formation of a complex array of components. The experiments on the *A*-nor alcohols (**6b,c,e,f**) were therefore abandoned.

The thermolyses of the ketones **6a** and **6d** did lead to definable products, however. Under optimal conditions (*n*-decane, 24 h at 140 °C, nitrogen), the 6*R* ketone **6a** produced *cis*-isotachysterone **11** (6%), previtamin ketone **12** (5%), recovered **6a** (2%), *trans*-isotachysterone **13** (35%) and spiro ketone[8] **14** (6%). Identical heating of the 6*S* ketone **6d** gave very similar results: **11** (~7%), **12** (~5%), recovered **6d** (~1%), **13** (39%), and **14** (~3%). The four products **11–14**, when separately thermolyzed under the reaction conditions, were observed to partially interconvert to varying degrees as well as rearrange to other components (high-pressure LC analyses). In order to assess the acid lability[9] of the vinylallene, treatment of **6a** with antimony trichloride[10] (room temperature, 18 h, chloroform) was found to afford **13** (18%), the diastereomeric (6*S*)-allene **6d** (20%), and recovered **6a** (13%).

As regards the structures of **11–14**, much information could be gained by comparison of their spectral data with those of closely related molecules in the six-membered A-ring series (**15–17**).[2a,d] Data for **11** and **15** and for **12** and **16** are directly compared in the supplementary material, and no further discussion is deemed necessary here. The structure of the major product **13** follows not only from comparison of its spectral data[11] with the corresponding data for its cis counterparts **11** and **15** but also from its formation from vinylallenone **6a** by acid catalysis. This acid-catalyzed isomerization process has an analogy to the well-known transformation of vitamin D_3 (**8b**) to isotachysterol **18**, a substance closely related to **13**.[10] The triene unit characteristic of **13** and **18** seems to be a thermodynamic sink for the vitamin D-like system. The structure of **14**, obtained in only small amounts, must be regarded as the most tentative. Its C_8 stereochemistry is uncertain, but its formation can be ascribed to a direct six-electron electrocyclization between C_8 and C_{19} of the putative *A*-norvitamin D ketone **7c**.[8] The formation of structural type **14** is rare and is precedented only by the recently reported **17**. The ultraviolet [λ_{max} 310 nm (ϵ 10 000)] and ^{1}H NMR spectra (olefinic AB quartet, τ 3.65 and 3.83, $J \approx 9.8$ Hz) of **14** are correspondingly similar to the data for **17** [λ_{max} 311 nm (ϵ 10 200); τ 3.85 and 4.15, $J \approx 10.0$ Hz].[2a]

Inspection of Dreiding models of the vinylallenes[12] reveals that the distances between the migrating hydrogen terminii, C_{19} and C_7, for a [1,5] sigmatropic shift differ significantly for the five- and six-membered-ring cases (**6** and **4**, respectively). These distances are 2.9 and 2.6 Å, respectively. This distance effect provides a simple rationale for the observation that the *A*-nor analogues (**6**) fail to arrange under the optimal conditions previously defined for the six-membered-ring cases (**4**). Under harsher conditions, the *A*-nor analogues undergo deep-seated rearrangement reactions, suggesting that the thermal thresholds for prototropic shifts[13] (and possibly dimerization, etc.) are lower than those for [1,5] sigmatropic shifts. Another possibility, of course, is that the desired [1,5] sigmatropic product(s) are labile to the reaction conditions.

In conclusion, the elevated temperatures and products associated with the thermolyses of the *A*-norvinylallenes define a structural limit to the vinylallene scheme. A new method must be generated for preparation of the *A*-norvitamin D analogues. Attempts are currently underway to further investigate this distance effect with the *A*-homo vinylallene series. The thermal conditions necessary to effect the [1,5] hydrogen shift for the latter are expected to be milder than those for the six-membered A-ring vinylallenes **4a–f** due to the closer estimated internuclear distance (2.4 Å) between the C_{19}-methyl and C_7-allene centers.

Experimental Section

General Methods. Ultraviolet (UV), infrared (IR), nuclear magnetic resonance, and mass spectra and other analytical data are summarized in the supplementary material. Dry ether refers to solvent freshly distilled under nitrogen from $LiAlH_4$ or K/benzophenone; lbpe refers to redistilled 30–60 °C low-boiling petroleum ether. It can be assumed that reactions involving air- and/or moisture-sensitive organometallic reagents were handled under a blanket of dry nitrogen. Air-sensitive polyolefins or allenes were normally stored in the cold under nitrogen. Semipreparative high-pressure liquid chromatography (HPLC) was carried out on a Waters 6000A solvent-delivery system equipped with a U6K injector and a dual detector system (UV at 2537 Å and a refractive index detector). A Whatman M9 10/50 Partisil (10μm) column (9.4 mm i.d. × 50 cm) was used. A Waters RCM-100 Module radial compression system with a silica (5μm) radial pack cartridge (5 mm i.d.) was used for analytical HPLC. Reagent grade ethyl acetate and Skellysolve B (distilled from CaH_2) were used as solvents. Solvents and solvent combinations for the Waters 6000 A system were normally vacuum filtered through a 0.45-μm Millipore filter immediately before use.

(6*R*)- (6a) and (6*S*)-*A*-Nor-9,10-secocholesta-5(10),6,7-trien-1-one (6d). A solution of the allenyllithium of hydrocarbon **9** was prepared as described previously[2d] from **9** (1.37 g, 5.0 mmol) in dry ether (38 mL) and *tert*-butyllithium (1.51 M in pentane, 3.48 mL, 5.25 mmol). An ether (13 mL) solution and 3-isobutoxy-2-methyl-2-cyclopentenone (**10**; 0.925 g, 5.5 mmol) was added (syringe, slow stream) to the cold (−78 °C), magnetically stirred solution of the allenyllithium solution. After 5 min, the bath was

(7) Mills, J. A. *J. Chem. Soc.* **1952**, 4976.

(8) The spiro thermolysis product **17** was isolated by heating a vinylallenone lacking the D ring.[2a]

(9) Treatment of **6a** under trifluoroacetic acid conditions (Dauben, W. G.; Chollet, A. *Tetrahedron Lett.* **1981**, 1583) afforded only starting material.

(10) Murray, T. K.; Day, K. C.; Kodicek, E. *Biochem. J.* **1966**, *98*, 293.

(11) The strongly red-shifted UV absorbance maximum at 337 nm is particularly significant (calculated 343 nm; see: Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. "Spectrometric Identification of Organic Compounds"; Wiley: New York, 1981; p 318). The ^{1}H NMR H_6–H_7 coupling constant is 16.5 Hz, characteristic of the *E* geometry.

(12) Bond angle corrected Dreiding models were used and the distances were measured for the 5,6-*s*-*cis* conformations of the vinylallenes. We thank Mr. Alberto Haces of this laboratory for suggesting the distance effect rationale.

(13) For the ketones **6a**, **6d**, and **11–14** one can readily envisage facile enolization of their cyclopentenone rings to cyclopentadienols. This could be followed by [1,5] hydrogen shifts and/or tautomerization to isomeric cyclopentenones as initial steps in more deep-seated shifts of the entire triene system. The lability of the products (**11–14**) to the reaction conditions of their formation from **6a** and **6d** (140 °C, 24 h) was certainly noted.

removed, and the mixture was stirred at ambient temperature for 1 h. Water was added, and the mixture was extracted thoroughly with ether. The ether extract was washed (water, brine), dried ($MgSO_4$), filtered, and then concentrated. The resulting viscous oil was chromatographed through a short column (25 × 170 mm; dry silica gel; lbpe, benzene, and then 5% acetone–benzene) to afford after concentration 1.72 g (93%) of a reasonably pure vinylallenone mixture (^1H NMR integration of the C-18 methyl group signal indicated the presence of a 12.2: 1 ratio of (6*R*)- to (6*S*)-allenes). Chromatography of the mixture on a 50 × 2 cm dry silica gel column (benzene) afforded first pure (6*S*)-allene **6d** (66.8 mg, 3.6%) and then second the major (6*R*)-allene **6a** (1.012 g, 55%).

Photolysis of (6*R*)-Vinylallenone 6a. An ice-cooled nitrogen-purged solution of (6*R*)-allene **6a** (0.987 g, 2.68 mmol) in isooctane (spectrograde, freshly distilled from $LiAlH_4$, 500 mL) was irradiated through quartz with a 100-W Hanovia medium-pressure lamp as previously described.[2d] Monitoring by HPLC or ^1H NMR indicated that a photostationary state (~1:1 ratio of 6*R* and 6*S* isomers) was reached within 15 min. Concentration and then chromatographic separation (75 × 2.5 cm dry silica column; benzene and then 2% acetone–benzene) afforded (6*S*)-allene **6d** (427.4 mg, 43%; 77% based on recovered 6*R* isomer) and (6*R*)-allene **6a** (434.2 mg, 44%).

(1*R*,6*R*)- (6b) and (1*S*,6*R*)-1-Hydroxy-*A*-nor-9,10-secocholesta-5(10),6,7-triene (6c). A solution (0 °C) of (6*R*)-*A*-nor-vinylallenone **6a** (169 mg, 0.46 mmol) in 0.4 M cerium(III) chloride heptahydrate/methanol solution (1.2 mL) was treated with $NaBH_4$ (17.1 mg, 0.46 mmol). After being stirred for 5 min, the mixture was warmed to room temperature and subjected to conventional processing (H_2O quench and then ether–water workup) to afford a 1:1 mixture of **6b** and **6c**. Semipreparative HPLC (10% ethyl acetate/Skellysolve B) followed by concentration and drying afforded spectrally and chromatographically pure **6b** (less polar; 79 mg, 46%) and **6c** (more polar; 66 mg, 39%). $LiAlH_4$ in ether gave similar results (34% **6b**, 30% **6c**), but $NaBH_4$ in methanol appeared to effect carbon–carbon double bond reduction.

(1*S*,6*S*)- (6f) and (1*R*,6*S*)-1-Hydroxy-*A*-nor-9,10-secocholesta-5(10),6,7-triene (6e). The $NaBH_4$–$CeCl_3$/methanol reduction of **6d** (45 mg, 0.12 mmol) was carried out exactly as described for **6a** in the preceding experiment. The crude mixture consisted of a 1:1 ratio of **6f** and **6e** (HPLC). Semipreparative HPLC afforded **6f** (less polar; 15 mg, 34%) and **6e** (more polar; 16 mg, 36%). $LiAlH_4$ in ether reduction gave similar results (27% **6f**, 37% **6e**), whereas $NaBH_4$ in methanol appeared to effect carbon–carbon double bond reduction.

Thermolysis of 6*R* Ketone 6a. A solution of 6*R* ketone **6a** (482 mg, 1.31 mmol) in freshly distilled *n*-decane (24 mL) was heated (140 °C, N_2) for 24 h. Monitoring by analytical HPLC (10% ethyl acetate/Skellysolve B) revealed that **6a** was nearly completely consumed after 24 h. Chromatographic removal of *n*-decane (short silica gel column, elution with lbpe and then 5% acetone/benzene), concentration, and then preparative HPLC (single injection, multiple shave/recycle) of the resulting residue under the same conditions yielded five significant fractions. Isolated in order of increasing elution time were **11** (31 mg, 6%), **12** (26 mg, 5%), 6*R* ketone **6a** (7 mg, 2%), **13** (169 mg, 35%), and **14** (29 mg, 6%). Each of the five components was obtained as an oil except 14 (amorphous foam). It was also noted that 6*S* ketone **6b** could not be detected as one of the products.

Thermolysis of 6*S* Ketone 6b. As described in the preceding experiment, thermolysis of **6b** (133 mg, 0.36 mmol; 10 mL of *n*-decane 140 °C, 24 h, N_2) and then a similar workup followed by semipreparative HPLC afforded in order of elution **11** (~9 mg, 7%), **12** (~6 mg, ~5%), **6b** (trace), **13** (52 mg, 39%), and **14** (~4 mg, ~3%).

Thermal Control Experiments of 11–14. In parallel experiments, **11** (2.0 mg), **12** (3.5 mg), **13** (6.0 mg), and **14** (3.5 mg) dissolved in *n*-decane (~1.0 mL) were heated (140 °C, N_2) for 24 h. Each separate thermolysis revealed by analytical HPLC (10% ethyl acetate/Skellysolve B) the presence of peaks (in varying ratios) with the same retention times as those of authentic specimens of **11–14** as well as other unidentified peaks. The complexity of the product mixtures precluded further studies on the positive identification of the components.

Acid Rearrangement of (6*R*)-*A*-Norvinylallenone 6a. A solution (25 °C, N_2) of (6*R*)-*A*-norvinylallenone **6a** (475 mg, 1.29 mmol) in chloroform (3 mL) was treated with a 20% (w/v) $SbCl_3/CHCl_3$ solution (30 mL) and stirred for 18 h. Quenching with 40% (w/v) tartaric acid/water (40 mL) and a conventional workup (lbpe and water extraction, $NaHCO_3$ wash) yielded a multicomponent crude oil (394 mg). Semipreparative HPLC (20% ethyl acetate/Skellysolve B; single injection, multiple shave/recycle) followed by concentration and drying of the appropriate fractions afforded in order of elution (6*S*)-vinylallenone **6d** (93 mg, 20%), starting (6*R*)-vinylallenone **6a** (63 mg, 13%), and *trans*-isotachysterone **13** (87 mg, 18%). Treatment of **6a** with a 50-mol excess of trifluoroacetic acid in methylene chloride for 1 h afforded only recovered starting material.

Acknowledgment. We are grateful to the National Institutes of Health (USPHS Grant AM-16595) for financial support. We thank Dr. M. Rappoldt of Philips-Duphar for generous gifts of vitamin D_3. We are also grateful to Dr. N. Cohen of Hoffman-LaRoche and Dr. U. Eder of Schering AG (Berlin, West Germany) for providing 2-methylcyclopentane-1,3-dione.

Registry No. 4a, 74398-26-8; **4b**, 67632-48-8; **4c**, 67670-78-4; **4d**, 74398-27-9; **4e**, 67670-79-5; **4f**, 67670-80-8; **6a**, 79421-01-5; **6b**, 79421-02-6; **6c**, 79421-03-7; **6d**, 79421-04-8; **6e**, 79421-05-9; **6f**, 79421-06-0; **9**, 74398-28-0; **10**, 22117-97-1; **11**, 79421-07-1; **12**, 79421-08-2; **13**, 79421-09-3; **14**, 79421-10-6.

Supplementary Material Available: Spectral and analytical data (13 pages). Ordering information is given on any current masthead page.

Reactions of Copper(I) Halide Complexes of Trivalent Phosphorus with Vinylic Halides[1]

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Received March 11, 1981

The direct formation of the vinylic carbon to phosphorus bond has been accomplished via reaction of vinylic halides with copper(I) halide complexes of trialkyl phosphites. In addition, formation of varying amounts of vinylic chlorides may be observed if the reaction is performed by using vinylic bromides with copper(I) chloride complexes of trialkyl phosphites. This halogen-exchange reaction may be made synthetically useful through the employment of copper(I) chloride complexes of triaryl phosphites or phosphines.

In support of a program of directed syntheses of organophosphorus compounds of potential biological activity,[2] it has been of interest to develop new methods for the generation of carbon–phosphorus bonds, in particular

0022-3263/81/1946-5200$01.25/0