afforded β-cyanoethyl-1,2-diphenylhydrazine, 78%, mp 122–123 °C, after recrystallization from benzene/pentane; MS m/z 237 (calcd for $C_{15}H_{15}N_3$, 237); ^1H NMR (60 MHz, $CDCl_3$) δ 2.73 (t, 2 H, J = 7 Hz), 3.83 (t, 2 H, J = 7 Hz), 5.67 (s br, 1 H), 6.7–7.4 (m, 10 H).

The products formed in CCl_4 are clearly indicative of free radical chemistry, and the faster rates in that solvent, relative to those for benzene, together with inhibition by persistent radicals in the latter medium strongly suggest radical chain chemistry in both solvents. Although the detailed mechanism(s) by which **1** and **2** decompose are still under investigation, we assume that radical chain induced decomposition, as suggested earlier for an analogue,[11] is involved. The gross features of that mechanism are illustrated in Scheme II for reaction of **2** in CCl_4.[12] Similar chain processes can account for their decomposition in benzene to cyanoalkanes and the hydro-β-cyanoalkylation of azobenzene with **1**.

Work on synthetic applications of **1** and **2** and on the reaction mechanisms (including the use of **2** as a source for "radical clock" experiments[10,13]) is in progress.

Acknowledgments are made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Natural Sciences and Engineering Research Council of Canada for support of this work.

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(11) (a) Yeung, D. W. K.; Warkentin, J. *Can. J. Chem.* **1976**, *54*, 1349. (b) *Ibid.* **1976**, *54*, 1345.

(12) The nature of the initiating step in these "self-starting" reactions is not known nor is the timing of the two C–N bond scissions known. At least one C–N bond must be breaking in concert with H abstraction ()C(OH)-N═N—R + R′· → R′H +)═O + ·N═NR) since abstraction of H to form an alkoxy radical intermediate is known to be too difficult (see ref 11). Fully concerted, induced decomposition is plausible also, for the two C–N bonds of a trans azo compound are correctly aligned for the concerted process.

(13) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 317.

Stereocontrolled Synthesis of Steroidal Side Chains

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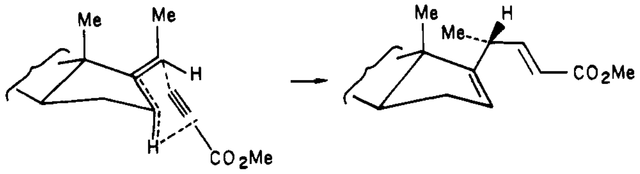
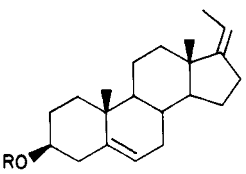
The introduction of the steroid side chain onto tetracyclic steroidal starting materials has been the subject of recent investigation by several research groups.[1,2] These efforts have been pursuing the introduction of functionalized side chains directed toward the synthesis of a variety of ecdysones,[3] vitamin D metabolites,[4] and unusual marine sterols.[5] We wish to report one of the most simple and efficient stereospecific syntheses of a steroidal side chain from $\Delta^{17(20)}$ steroid. This approach makes use of the known preference for attack on the α face of the C-17(20) double bond[6] and the highly ordered transition state of the ene reaction to set the stereochemistry of the C-20 carbon in the natural configuration (see Scheme I).

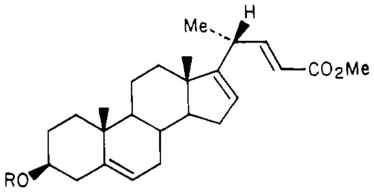
Scheme I



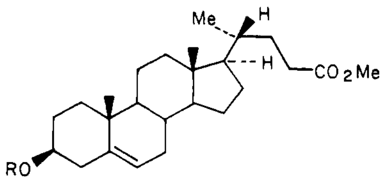
Diene **1**[7] was allowed to react with 1.2 equiv of methyl propiolate and 2.0 equiv of diethylaluminum chloride[8] in benzene for 24 h at room temperature. The reaction mixture was treated with an aqueous sodium bicarbonate solution and then extracted with ether to afford triene **3**[9] (95%), mp 128–129 °C; $[\alpha]_D$ ($CHCl_3$) −24.0°; IR ($CHCl_3$) 1720, 1650, 1020, and 980 cm^{-1}; NMR ($CDCl_3$) δ 1.17 (d, 3, J = 6 Hz, 21-H), 5.40 (dd, 2), 5.80 (dd, 1, J = 1.5, 16 Hz), 6.90 (dd, 1, J = 8, 16 Hz).



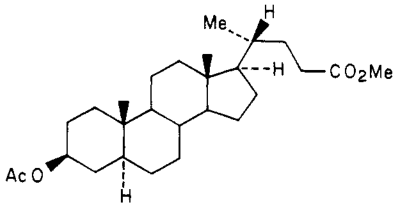
1, R = Ac
2, R = H



3, R = Ac
4, R = H



5, R = Ac
6, R = H



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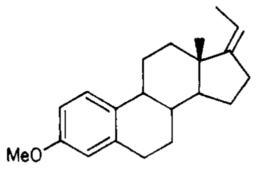

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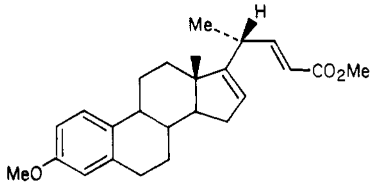

9

In order to prove the structure of triene **3**, especially the natural configuration at C-20, the reaction product was selectively hydrogenated with palladium on calcium carbonate in ethyl acetate to **5** (98%), mp 162–163 °C (lit.[10] 159–161 °C). The spectral data from this compound were identical with those previously reported.[10] Also the melting point of a mixture of **5** and authentic

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†NIH Postdoctoral Fellow, 1979–1981.

(1) For a review on steroid side chain homologation, see: Piatak, D. M.; Wicha, J. *Chem. Rev.* **1978**, *78*, 199.

(2) (a) Trost, B. M.; Matsumura, Y. *J. Org. Chem.* **1977**, *42*, 2036. (b) Trost, B. M.; Verhoeven, T. K. *J. Am. Chem. Soc.* **1978**, *100*, 3435. (c) Trost, B. M.; Bernstein, P. R.; Funfschilling, P. C. *Ibid.* **1979**, *101*, 4378. (d) Grieco, P. A.; Tukigawa, T.; Moore, D. R. *Ibid.* **1979**, *101*, 4380. (e) Schow, S. R.; McMorris, T. C. *J. Org. Chem.* **1979**, *44*, 3760. (f) Koreeda, M.; Tanaka, Y.; Schwartz, A. *Ibid.* **1980**, *45*, 1172. (g) Tanabe, M.; Hayashi, K. *J. Am. Chem. Soc.* **1980**, *102*, 862. (h) Midland, M.; Kwon, Y., private communication.

(3) (a) Nakanishi, K. *Pure Appl. Chem.* **1971**, *25*, 167. (b) Hikino, H.; Hikino, Y. *Fortschr. Chem. Org. Naturst.* **1970**, *28*, 256.

(4) (a) DeLuca, H. F.; Schnoes, H. K. *Annu. Rev. Biochem.* **1976**, *45*, 631. (b) Georghiou, P. E. *Chem. Soc. Rev.* **1977**, *6*, 85.

(5) (a) Nes, W. R.; McKean, M. L. "Biochemistry of Steroids and Other Isoprenoids"; University Park Press: Baltimore, MD, 1977. (b) Minale, L.; Sodano, G. In "Marine Natural Products Chemistry"; Faulkner, D. J., Fenical, W. H., Eds.; Plenum Press: New York, 1977, p 87.

(6) (a) Krubiner, A. M.; Oliveto, E. P. *J. Org. Chem.* **1966**, *31*, 24. (b) Krubiner, A. M.; Gottfried, N.; Oliveto, E. P. *Ibid.* **1968**, *33*, 1715.

(7) Drefahl, G.; Ponsold, K.; Schick, H. *Chem. Ber.* **1965**, *98*, 604.

(8) The use of mild Lewis acids to catalyze ene reactions has been previously reported: Snider, B. B.; Rodini, D. J.; Conn, R. S. E.; Sealfon, S. *J. Am. Chem. Soc.* **1979**, *101*, 5283.

(9) Spectroscopic data and elemental composition in full accord with the assigned structure have been obtained. The C NMR spectra of **3**, **4**, **5**, **7**, and **9** showed the expected number of signals. Of particular importance is the presence of only one absorption for the C-18 methyl group, the values being δ 16.17, 16.42, 11.88, 12.17, and 16.55, respectively.

(10) Vanderah, D. J.; Djerassi, C. *J. Org. Chem.* **1978**, *43*, 1442.

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material, prepared[11] from (20*R*)-3β-hydroxy-5-cholenic acid (**6**)[12] showed no depression. As further proof, hydrogenation of triene **3** with palladium on carbon in ethanol yielded hexahydro ester **7**[9] (97%), mp 159–160 °C (lit.[10] 159–160 °C). The spectral data from this compound were also identical with those previously reported,[10] and the melting point of a mixture of **7** and authentic material prepared by hydrogenation of the natural cholenic acid derivative **5** showed no depression. These data prove conclusively that the *R* configuration assigned at C-20 is correct.

The corresponding 3β-hydroxy compound (**2**) afforded the analogous ene product (**4**), stereospecifically in 95% yield. Although this material did not exhibit a sharp melting point (80–90 °C) after repeated recrystallizations (due perhaps to polymorphism or hygroscopic tendencies), its spectral data supports the proposed structure. In addition, treatment of **4** with acetic anhydride at reflux for 2 h produced material in 85% yield which was identical with triene **3**, and a melting point of a mixture of these products exhibited no depression.

The same reaction conditions were employed to convert the ethylidene derivative of estrone methyl ether **8**[6] via the ene reaction to ester **9**[9] (90%): mp 83–84 °C; IR ($CHCl_3$) 1710, 1650, 1610, 1020, and 980 cm^{-1}; NMR ($CDCl_3$) δ 1.20 (d, 3, J = 8 Hz, 21-H), 5.40 (dd, 1), 5.80 (dd, 1, J = 1.5, 16 Hz), 6.90 (dd, 1, J = 8, 16 Hz).

Of all the published procedures,[1,2] this process is the most direct and highest yielding stereospecific method for the attachment of a steroidal side chain and is the only process which has been reported to proceed directly on an unprotected, unsaturated steroidal alcohol.

Acknowledgment. This work was supported by Grant No. AM 00709, National Institute of Arthritis, Metabolism, and Digestive Diseases.

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(11) Wallis, E. S.; Fernholz, E. *J. Am. Chem. Soc.* **1935**, *57*, 1504.

(12) This material was generously supplied by Dr. M. Tanabe, Stanford Research Institute.

Alkylidene Complexes from the Reactions of Transition-Metal Dianions with Iminium Salts: Synthesis and Spectral Characterization of [Mo(CO)$_5$CPh$_2$]

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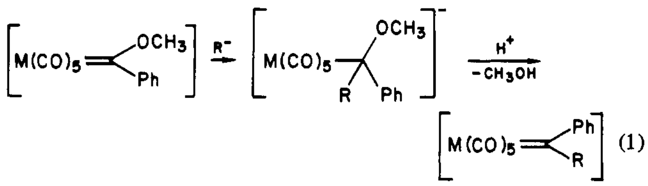
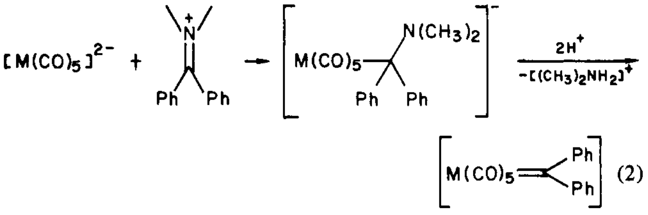
Important recent developments in the chemistry of the transition metal to carbon double bond have included syntheses of alkylidene complexes, in a variety of metal–ligand environments, lacking the stabilizing heteroatomic substituents characteristic of the carbene complexes prepared by Fischer and others.[1–3] A notable early example of such a complex was [W(CO)$_5$CPh$_2$],[1c] prepared from an alkoxycarbene complex as shown in eq 1 (R = Ph). Subsequent studies of the reactions of this species with alkenes[4] have had an important influence on the development of current ideas about the mechanism of the alkene metathesis reaction and focused considerable attention on the chemistry of this and related species. Fischer has reported independent syntheses of related W and Cr complexes[1f] and the successful isolation of one of the intermediate tungstates,[1g] and Casey has also prepared thermally unstable monoarylalkylidenes in this metal–ligand environment (eq 1, R = H, Me).[1d,e]



(1)

We wish to report the synthesis and characterization of a new alkylidene complex, [Mo(CO)$_5$CPh$_2$], which, together with the species [M(CO)$_5$CPh$_2$] (M = Cr, W), provides the first example of the isolation of a set of isologous alkylidene complexes containing each of the metals of a d-block triad. The preparation of the complex (eq 2, M = Mo) involves nucleophilic attack of a transition-metal dianion on an imminium salt to give an (aminomethyl)metalate, closely related to the (alkoxymethyl)metalate in eq 1, which can be deaminated to give the alkylidene. We have demonstrated the potential of sequences of this type as general routes to alkylidene complexes by preparing the Cr and W analogues of the Mo complex in a similar manner (eq 2, M = Cr, W).



(2)

Addition of 3.38 mmol of powdered [Ph$_2$CNMe$_2$][OSO$_2$F][5] to a solution of 3.52 mmol[6] of Na$_2$[Mo(CO)$_5$] in 25 mL of tetrahydrofuran (THF)[7] at −78 °C resulted in a smooth reaction to give, after 1 h, a red-purple solution containing only traces of suspended solid. The solution changed color to light amber after addition of 28.3 mmol of CF$_3$CO$_2$H at −78 °C and was then warmed to −35 °C. At this temperature a slow reaction occurred to give, after 3 h, an intensely colored red solution containing the product alkylidene complex. Excess acid was neutralized by

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(1) For alkylidene syntheses, see: (a) Öfele, K. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 950. (b) Sanders, A.; Cohen, L.; Giering, W. P.; Kenedy, D.; Magatti, C. V. *J. Am. Chem. Soc.* **1973**, *95*, 5430. (c) Casey, C. P.; Burkhardt, T. J.; Bunnell, C. A.; Calabrese, J. C. *Ibid.* **1977**, *99*, 2127. (d) Casey, C. P.; Polichnowski, S. W.; Shusterman, A. J.; Jones, C. R. *Ibid.* **1979**, *101*, 7282. (e) Casey, C. P.; Albin, L. D.; Burkhardt, T. J. *Ibid.* **1977**, *99*, 2533. (f) Fischer, E. O.; Held, W.; Kreissl, F. R.; Frank, A.; Huttner, G. *Chem. Ber.* **1977**, *110*, 656. (g) Fischer, E. O.; Held, W.; Kreissl, F. R. *Ibid.* **1977**, *110*, 3842. (h) Brookhart, M.; Nelson, G. O. *J. Am. Chem. Soc.* **1977**, *99*, 6099. (i) Fischer, E. O.; Clough, R. L.; Besl, G.; Kreissl, F. R. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 543. (j) Fischer, E. O.; Clough, R. L.; Stuckler, P. *J. Organomet. Chem.* **1976**, *120*, C6. (k) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98 and references therein.

(2) We adhere to the convention[1k] of referring to complexes with α-heteroatomic substituents as carbene complexes and those lacking such substituents as alkylidene complexes.

(3) For reviews of carbene complexes, see: (a) Fischer, E. O. *Pure Appl. Chem.* **1972**, *30*, 353. (b) *Ibid.* **1970**, *24*, 407. (c) Cardin, D. J.; Cetinkaya, B.; Lappert, M. F. *Chem. Rev.* **1972**, *72*, 545. (d) Cardin, D. J.; Cetinkaya, B.; Doyle, M. J.; Lappert, M. F. *Chem. Soc. Rev.* **1973**, *2*, 99. (e) Fischer, E. O. *Pure Appl. Chem.* **1978**, *50*, 857. (f) Cotton, F. A.; Lukehart, C. M. *Prog. Inorg. Chem.* **1972**, *16*, 487.

(4) (a) Casey, C. P.; Burkhardt, T. J. *J. Am. Chem. Soc.* **1974**, *96*, 7808. (b) Katz, T. J.; McGinnis, J.; Altus, C. *Ibid.* **1976**, *98*, 606. (c) McGinnis, J.; Katz, T. J. Hurwitz, S. *Ibid.* **1976**, *98*, 605.

(5) Readily prepared by condensing benzophenone with methylamine to form Ph$_2$CNMe and methylating this imine with MeOSO$_2$F in CH$_2$Cl$_2$: Tennant, G. In "Comprehensive Organic Chemistry"; Sutherland, I. O., Ed.; Pergamon Press: Elmsford, NY, 1979; Vol. 2, p 385.

(6) Based on the quantity of amine complex used to prepare the dianion.[7]

(7) Na$_2$[W(CO)$_5$],[8] Na$_2$[Mo(CO)$_5$],[8] Na$_2$[Cr(CO)$_5$],[9] and Li$_2$[W(CO)$_5$] can be obtained in high yield and purity as THF solutions by reduction of [M(CO)$_5$(NMe$_3$)] (M = Cr, Mo, W) with the appropriate alkali naphthalide. Details of the preparation of these and other transition-metal dianions will be published shortly: Maher, J. M.; Beatty, R. P.; Cooper, N. J., manuscript in preparation.

(8) (a) Ellis, J. E.; Hagen, G. P. *Inorg. Chem.* **1977**, *16*, 1357. (b) Ellis, J. E.; Hagen, G. P. *J. Am. Chem. Soc.* **1974**, *96*, 7525.

(9) Ellis, J. E.; Hentges, S.; Kalina, D.; Hagen, G. P. *J. Organomet. Chem.* **1975**, *97*, 79.

0002-7863/81/1503-238$01.00/0