7b, 119694-27-8; **7c**, 119694-36-9; **7d**, 119694-29-0; **8a**, 119694-22-3; **8b**, 119694-24-5; **8c**, 119694-25-6; **10a**, 119694-30-3; **10b**, 119694-31-4; **10c**, 119694-32-5; **18**, 119694-23-4; **19**, 119694-33-6; **20**, 119720-72-8; 4-bromobutene, 5162-44-7; methyl 3,5-dimethylbenzoate, 25081-39-4; 1-bromo-3-methylbutene, 20038-12-4; 1-bromo-4-methyl-3-pentene, 2270-59-9; benzonitrile, 140-29-4; methyl benzoate, 93-58-3; 3-(3'-butenyl)-1,5-dimethyl-3-(methoxycarbonyl)-1,4-cyclohexadiene, 119694-07-4; 1,5-dimethyl-3-(methoxycarbonyl)-3-(3'-methyl-3'-butenyl)-1,4-cyclohexadiene, 119694-08-5; 1,5-dimethyl-3-(4'-methyl-3'-pentenyl)-3-(methoxy carbonyl)-1,4-cyclohexadiene, 119694-09-6; 3-(3'-butenyl)-3-cyano-1,4-cyclohexadiene, 119694-10-9; 3-(3'-butenyl)-3-(methoxycarbonyl)-1,4-cyclohexadiene, 119694-11-0; 3-(3'-butenyl)-1,5-dimethyl-3-(hydroxymethyl)-1,4-cyclohexadiene, 119694-12-1; 1,5-dimethyl-3-(hydroxymethyl)-3-(3'-methyl-3'-butenyl)-1,4-cyclohexadiene, 119694-13-2; 1,5-dimethyl-3-(hydroxymethyl)-3-(4'-methyl-3'-pentenyl)-1,4-cyclohexadiene, 119694-14-3; 3-(3'-butenyl)-3-(hydroxymethyl)-1,4-cyclohexadiene, 119694-15-4; 3-(acetoxymethyl)-3-(3'-butenyl)-1,5-dimethyl-1,4-cyclohexadiene, 119694-16-5; 3-(acetoxymethyl)-1,5-dimethyl-3-(3'-methyl-3'-butenyl)-1,4-cyclohexadiene, 119694-17-6; 3-(acetoxymethyl)-1,5-dimethyl-3-(4'-methyl-3'-pentenyl)-1,4-cyclohexadiene, 119694-18-7; 3-(acetoxymethyl)-3-(3'-butenyl)-1,4-cyclohexadiene, 119694-19-8.

Scope and Regiochemical Control of the Allylpotassium Reaction in the Synthesis of Sterols with Unsaturated Side Chains

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Allylpotassium derivatives were prepared from a variety of olefins by using Schlosser's base (BuLi/KOt-Bu). Reaction with (20*S*)-20-(iodomethyl)pregnane *i*-methyl ether (**1**) followed by deprotection gave in high yields a wide variety of Δ^{24} and $\Delta^{24(28)}$ sterols, including the naturally occurring desmosterol (**37**), fucosterol (**33**), 24(*E*)-propylidenecholesterol (**35**), 24-methylenecholesterol (**3**), dehydroaplysterol (**10**), 25-methyl-24-methylenecholesterol (**11**), mutasterol (**12**), and 25-methylxestosterol (**13**). Control of the regiochemistry of unsymmetrical allylmetals was achieved through the addition of Li_2CuCl_3. Rules concerning the high regioselectivities and stereoselectivities are discussed.

Sterols containing the Δ^{24} and $\Delta^{24(28)}$ double bond are common in nature and represent key intermediates in sterol biosynthesis.[1] In this paper we present our application of allylpotassium compounds[2] to the synthesis of a wide variety of such unsaturated sterol side chains from simple olefins and a common steroidal precursor.

It has become increasingly necessary in our biosynthetic studies of sterols of marine origin[3] to be able to synthesize a wide variety of sterol side chains as precursors in feeding experiments, for structure proofs, and as cold carriers for the chromatographic and degradative analyses of feeding experiments. With the allylmetal method we describe a means by which a great number of sterols containing unsaturated side chains may be conveniently prepared in high yields by a single reaction.

Results and Discussion

Our initial success in the coupling the steroidal iodide **1**[4] with the allylpotassium derived by deprotonation of 2,3-dimethyl-1-butene (**2**) with Schlosser's base[2] (BuLi/KOt-Bu) to give the *i*-methyl ether of 24-methylenecholesterol (**3**)[5] (Figure 1) prompted further investigation of this procedure with results summarized in Table I.

Substitution of the Δ^7 iodide (**4**) for **1** gave the protected Δ^7 24-methylene sterol (**5**). Reaction of the *i*-methyl iodide **1** with the allylpotassiums derived from 2,3-dimethyl-1-pentene (**6**) and especially the olefins **7–9** containing quaternary centers gave aplysterol (**10**),[6] 25-methyl-24-methylenecholesterol (**11**),[7] mutasterol (**12**),[8] and 25-methylxestosterol (**13**)[9] as their *i*-methyl ethers in good yields (72–95%). Regeneration of the Δ^5-3β-hydroxy moiety was then accomplished in high yield by the conventional procedure.[4] In this series, the yield of the reaction decreased with increasing steric hindrance (Table I). The steric hindrance of the tertiary amyl group in **12** and the yet bulkier group in **13** has been a problem leading to low yields in our previous syntheses of **12**[8] and **13**[9] by aldol condensations followed by Wittig reaction of the resulting ketones. Allylpotassiums derived from isobutylene (**14**) and propylene (**15**) gave the unnatural sterols **16** and **17** with shortened side chains.[10]

The regiochemical outcome of the reactions of unsymmetrical allylpotassiums generated from olefins **18–32** can be seen in Table II: attack at both termini of the allyl system gives rise to sterols **33–68** with a preference for attack at the less substituted terminus. Provided that the products are easily separable, this can be a satisfactory way of preparing certain sterols. For instance desmosterol

(1) (a) Goodwin, T. W. In *Biosynthesis of Isoprenoid Compounds*; Porter, J. W., Spurgeon, S. L., Eds.; Wiley: New York, 1981; Vol. 1, pp 443–480. (b) Goodwin, T. W. In *The Enzymes of Biological Membranes*; Martonosi, A. N., Ed.; Plenum: New York, 1984; Vol. 2, pp 205–226.

(2) (a) Schlosser, M. *J. Organomet. Chem.* **1967**, *8*, 9–16. (b) Schlosser, M.; Strunk, S. *Tetrahedron Lett.* **1984**, *25*, 741–744. (c) Hartmann, J.; Schlosser, M. *Helv. Chim. Acta* **1976**, *59*, 453–466.

(3) Stoilov, I. L.; Thompson, J. E.; Cho, J.-H.; Djerassi, C. *J. Am. Chem. Soc.* **1986**, *108*, 8235–8241 and references cited therein.

(4) Partridge, J. J.; Faber, S.; Uskokovic, M. R. *Helv. Chim. Acta* **1974**, *57*, 764–771.

(5) Back, T. G.; Proudfoot, J. R.; Djerassi, C. *Tetrahedron Lett.* **1986**, *27*, 2187–2190.

(6) Catalan, C. A. N.; Thompson, J. E.; Kokke, W. C. M. C.; Djerassi, C. *Tetrahedron* **1985**, *41*, 1073–1084.

(7) (a) Akihisa, T.; Shimizu, N.; Ghosh, P.; Thakur, S.; Rosenstein, F. U.; Tamura, T.; Matsumoto, T. *Phytochemistry* **1987**, *26*, 1693–1700. (b) Kim, S. K.; Akihisa, T.; Tamura, T.; Matsumoto, T.; Yokota, T.; Takahashi, N. *Phytochemistry* **1988**, *27*, 629–631.

(8) Li, L. N.; Sjöstrand, U.; Djerassi, C. *J. Am. Chem. Soc.* **1981**, *103*, 115–119.

(9) Li, L. N.; Sjöstrand, U.; Djerassi, C. *J. Org. Chem.* **1981**, *46*, 3867–3870.

(10) Massey, I. J.; Djerassi, C. *J. Org. Chem.* **1979**, *44*, 2448–2456.

0022-3263/89/1954-2117$01.50/0

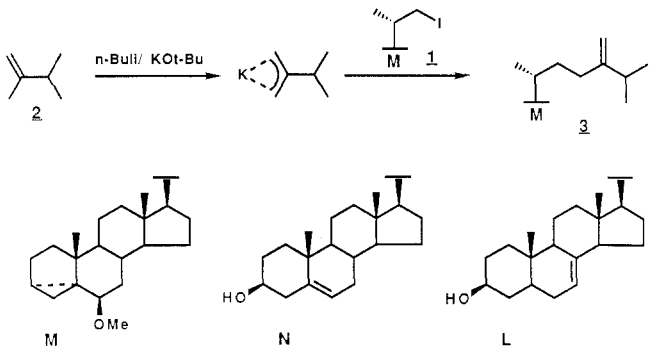


Figure 1. Synthesis of 24-methylenecholesterol *i*-methyl ether (**3**) via allylpotassium from 2,3-dimethyl-1-butene (**2**).

Table I. Synthesis of 24-Methylenecholesterol *i*-Methyl Ethers via Symmetrical Potassium Allyls

olefin	product	yield, %
2	3	98
2[a]	5	85
6	10	95
7	11	88
8	12	84
9	13	72
14	16	100
15	17	91

[a] Reaction with steroidal iodide 4.

4

i-methyl ether (**37**)[11] can be readily separated from its regioisomer **38**[11a,b] by argentic silica gel column chromatography. The 67% yield and the simplicity of the reaction compares very favorably to a recently published synthesis[11c] (38% overall yield) of this biosynthetically important compound. However, as shown below (cf. Table IV), the formation of the minor regioisomer can be eliminated completely by new experimental modifications.

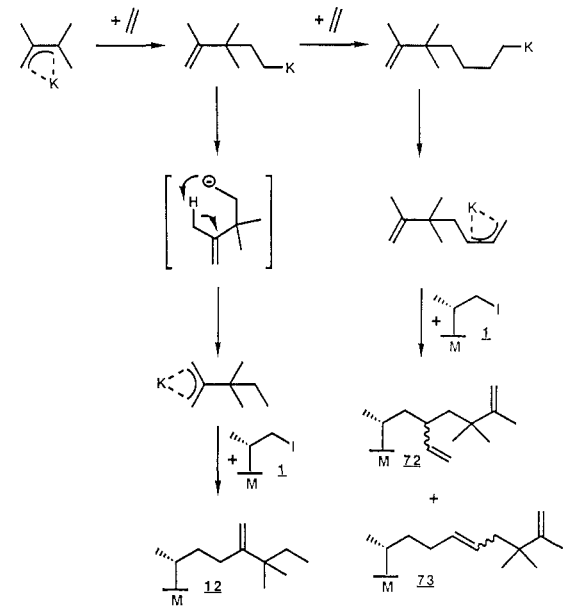


Figure 2. Possible origin of side products in the reaction of allylpotassium of 2,3-dimethyl-2-butene (**26**) and (20*S*)-20-(iodomethyl)pregnane *i*-methyl ether (**1**).

The minor products of the nonregioselective reactions are often also useful. When small samples are required for structure proofs or as analytical standards for biosynthetic experiments, a low yield in a one-step reaction may be quite acceptable. For example, the spectroscopic data of either isomer of **36**, the minor product derived from **19**, do not match that reported for a sterol isolated from a Chinese soft coral,[12] to which this unusual structure had been assigned. In many cases the convenience of the reaction as a preparative method outweighs the low yield of the minor product. For instance, when the homologous steroidal iodide **69**[13] is reacted with the anion of 2-methyl-2-pentene (**22**) the minor product (epi)clerosterol (**44**) is obtained in 22% yield. Although the final purification requires HPLC, this is a simple and direct method for the preparation of a mixture of both epimers of this biosynthetically important sterol and may represent an improvement over other syntheses in terms of convenience.[14] In a similar fashion, **54**, the Δ^5 analogue of an unusual Δ^7 sterol recently isolated from a higher plant,[15] was prepared.

Mechanistically interesting compounds were isolated from the reaction of 2,3-dimethyl-2-butene (**26**) (Table III). The large sterol electrophile made the observation of previously undescribed side products possible, which are much more difficult to detect and isolate when smaller, more volatile, electrophiles such as methyl iodide or ethylene oxide are allowed to react with the organometallic. Side products **70**, **71**, **74**, **75**, and **45–47** were also found in the reactions of many of the other olefins, though to a lesser extent. Formation of products **70** and **71**[16] can be accounted for by reduction or transmetalation and β-elimination of the steroidal synthon, while Wurtz-type coupling of the iodide gives rise to **74**. Products **45–47**

(11) (a) Apfel, M. A. *J. Org. Chem.* **1978**, *43*, 2284–2285. (b) Morisaki, M.; Shibata, M.; Duque, C.; Imamura, N.; Ikekawa, N. *Chem. Pharm. Bull.* **1980**, *28*, 606–611. (c) Kircher, H. W.; Rosenstein, F. U. *J. Org. Chem.* **1987**, *52*, 2586–2588.

(12) Lai, Z.; Long, K. *Zhongshan Daxue Xuebao, Ziran Kexueban* **1985**, 110–111; *Chem. Abstr.* **1985**, *102*, 76016e.

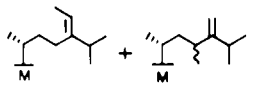
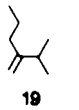
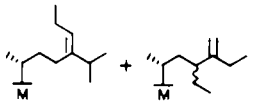
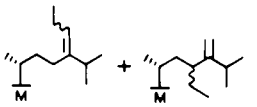
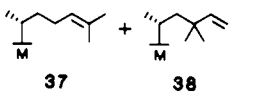
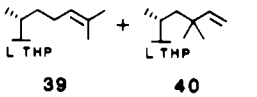
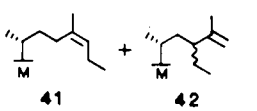
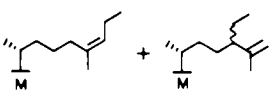
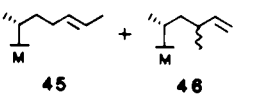
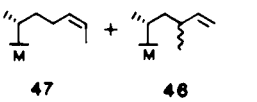
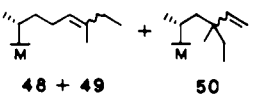
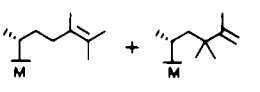
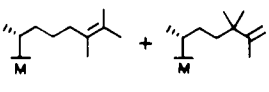
(13) Theobald, N.; Wells, R. J.; Djerassi, C. *J. Am. Chem. Soc.* **1978**, *100*, 7677–7684.

(14) Schow, S. R.; McMorris, T. C. *J. Org. Chem.* **1979**, *44*, 3760–3765.

(15) Ahihisa, T.; Shimizu, N.; Tamura, T.; Matsumoto, T. *Lipids* **1986**, *21*, 515–517.

(16) Brunke, E.-J. *Tetrahedron* **1979**, *35*, 781–788.

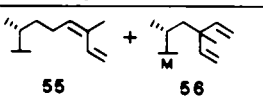
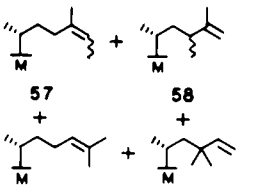
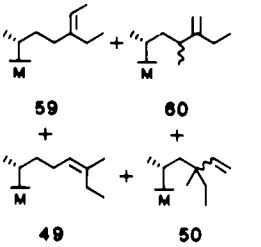
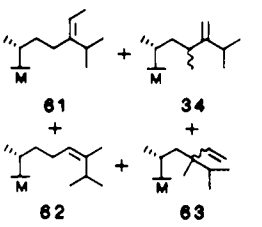
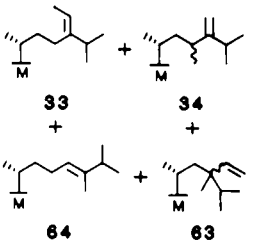
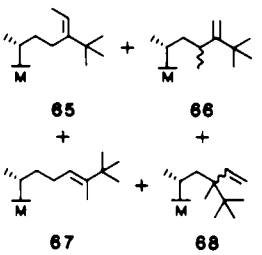
Table II. Products of Reaction of Allylpotassiums Derived from Various Olefins with (20*S*)-20-(Iodomethyl)pregnane *i*-Methyl Ether (1)

olefin	products	yield, %, ratio
 18	 33 + 34	98, 64/36
 19	 35 + 36	81, 73/27
 20	 35 + 36	64, 73/27 (*E*/*Z* 3:1)
 21	 37 + 38	87, 77/23
 [a] 21	 39 + 40	73, 77/23
 22	 41 + 42	82, 72/28
 [b] 22	 43 + 44	80, 72/28
 23	 45 + 46	68, 66/34
 24	 47 + 46	56, 66/34
 25	 48 + 49 + 50	70, 79/21 (*E*/*Z* 5:1)
 [c] 26	 51 + 52	9, 68/32
 [b] 26	 53 + 54	17, 67/33

[a] Reaction with steroidal iodide 4.  4

[b] Reaction with steroidal iodide 69.  69

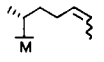
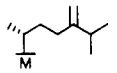
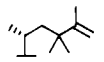
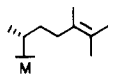
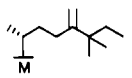
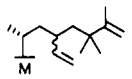
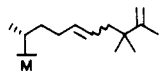
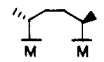
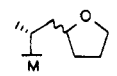
[c] See Table IV for complete analysis.

olefin	products	yield, %, ratio
 27	 55 + 56	96, 71/29
 28	 57 + 58 + 37 + 38	43/32 (*E*/*Z* 3:1) 66 17/8
 29	 59 + 60 + 49 + 50	68 24/12 46/18
 30	 61 + 34 + 62 + 63	42 11/3 80/6
 31	 33 + 34 + 64 + 63	57 39/15 41/5
 32	 65 + 66 + 67 + 68	40 20/10 65/5

probably arise from butenylpotassium, which is formed from the butylmethyl by β-elimination followed by deprotonation of the resulting butene. Equilibration of the allyl species derived from **26** via protonation and deprotonation may give rise to **3**.[2c] Mutasterol (**12**) is considered to arise via ethylene insertion[17] followed by what may be an intramolecular deprotonation to give a new allyl anion (Figure 2). Ethylene is known to arise through decom-

(17) (a) Schlosser, M.; Schneider, P. *Helv. Chim. Acta* **1980**, *63*, 2404-2410. (b) Margot, C. Doctoral Thesis, Swiss Federal Institute of Technology, Lausanne, 1985.

Table III. Products of the Reaction of the Allylpotassium of 2,3-Dimethyl-2-butene (26) with (20*S*)-20-(Iodomethyl)pregnane *i*-Methyl Ether (1)

 **70**	1.4%
 **71**	6.0%
 **46**	0.3%
 **47,45**	0.6% (*E*/*Z* 1:2)
 **3**	0.2%
 **52**	2.8%
 **51**	6.2%
 **12**	11.5%
 **72**	0.3%
 **73**	1.9%
 **74**	46%
 **75**	21%
	98.2% total yield

position of α-metalated THF.[18] An unprecedented double ethylene insertion can give rise to **72** and **73**. Reaction of the iodide with the α-metalated THF[18] gives **75**. The isolation of the THF derivative is remarkable and sheds new light on the stability of this reputedly unstable species at −50 °C.

Products of formal double ethylene insertion at the disubstituted terminus of the allylpotassium were also detected in the reactions of 3-methyl-1-butene (**21**) and 3-methyl-1-pentene (**25**). In these cases, however, single ethylene insertion was not detected since it cannot lead to a new reactive allyl species. In order to prove that the extra ethyl group in mutasterol (**12**) is derived from ethylene formed from THF, the reaction with 2,3-dimethyl-2-butene (**26**) was carried out in perdeuterated

(18) Lehman, R.; Schlosser, M. *Tetrahedron Lett.* **1984**, *25*, 745–748.

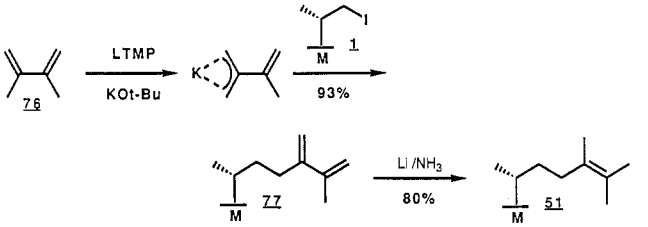


Figure 3. Synthesis of 24-methyldesmosterol *i*-methyl ether (**51**) via the allylpotassium of 2,3-dimethylbutadiene (**76**).

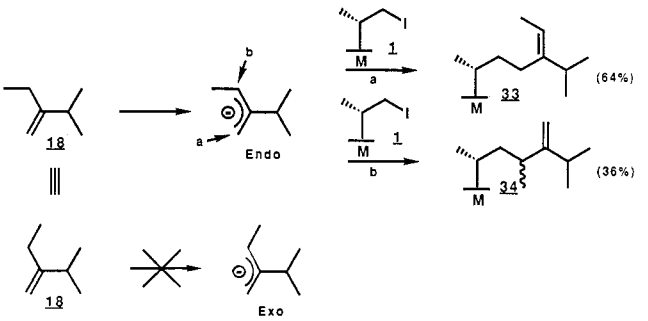


Figure 4. Formation and reactivity of the allylpotassium from olefin 18.

THF. Four deuterium atoms were incorporated into mutasterol (**12**) through the insertion reaction of perdeuterated ethylene, but its yield was reduced (and that of the products of double insertion **72** and **73** completely suppressed) due to a substantial isotope effect. Decomposition of the solvent as determined by ethylene insertion products could be minimized somewhat by forming BuLi/KOt-Bu in the presence of the olefin and carefully controlling the temperature. No other solvents besides diethyl ether, which is not suitable, were explored. The ethylene insertion reaction may provide a synthetically useful route to mutasterol (**12**) if the olefin **8**, employed in the high-yield synthesis (Table I) of mutasterol, is not available. The 11% yield of **12** via the ethylene insertion reaction (Table III and Figure 2) is still better than that recorded in the literature.[8] Optimization was not attempted, but direct addition of ethylene to the reaction mixture may provide a means of improving this reaction.[17b]

An alternative route to 24-methyldesmosterol *i*-methyl ether (**51**)[19] in greatly improved yield was provided via the anion of 2,3-dimethylbutadiene (**77**) (Figure 3). In this case BuLi/KOt-Bu gave a large amount of polymeric products. When lithium tetramethylpiperidide (LTMP) activated by KOt-Bu was used as the base,[20] the *i*-methyl ether of ergosta-5,24(28),25-trien-3β-ol[21] (**77**) was obtained in excellent yield. Birch reduction of the diene generated the 24-methyldesmosterol (**51**) side chain in good yield.

On the basis of the variety of allylpotassium reactions summarized in Table II and the work of Schlosser et al.,[22,23] some generalizations can be made to assist the application of this synthetically useful reaction:

(19) (a) Lockley, W. J. S.; Roberts, D. P.; Rees, H. H.; Goodwin, T. W. *Tetrahedron Lett.* **1974**, 3772–3776. (b) Li, H. T.; Djerassi, C. *J. Org. Chem.* **1982**, *47*, 4298–4303.

(20) (a) Klusener, P. A. A.; Hommes, H. H.; Verkruijsse, H. D.; Brandsma, L. *J. Chem. Soc., Chem. Commun.* **1985**, 1677–1678. (b) Klusener, P. A. A.; Kulik, W.; Brandsma, L. *J. Org. Chem.* **1987**, *52*, 5261–5266.

(21) Gebreyesus, T.; Stoilov, I.; Luo, F.-T.; Djerassi, C. *Steroids* **1985**, *45*, 447–451.

(22) (a) Schlosser, M.; Hartmann, J.; David, V. *Helv. Chim. Acta* **1974**, *57*, 1567–1576. (b) Stähle, M.; Hartmann, J.; Schlosser, M. *Helv. Chim. Acta* **1977**, *60*, 1730–1738.

(23) Schlosser, M.; Hartmann, J. *J. Am. Chem. Soc.* **1976**, *98*, 4674–4676.

The configuration of the double bond is maintained in the "stereodefensive" deprotonation,[22b] as shown in the reaction of (*E*)-2-butene (**23**) and (*Z*)-2-butene (**24**). When a mixture of double bond isomers of 2,3-dimethyl-3-hexene (**20**) was used, a mixture of double bond isomers in the product (**35**) was encountered.

The observed carbon acidity sequence under these conditions is $CH_3 > CH_2 > CH$.

There is a strong preference for the endo *Z* conformation[22,23] of the allylpotassium, which has been attributed to intramolecular hydrogen bonding.[23] It is worth noting that the complete selectivity in the syntheses of fucosterol (**33**) and 24-propylidenecholesterol (**35**) results from preferred deprotonation of a rotational conformer of the olefin (Figure 4). This endo selectivity was used to assign the cis stereochemistry of the double bond to products **41** and **57a**. In the case of the diene **27**, the cis configuration of product **55** is assigned on the basis of a "U"-shaped anion.[24]

The pattern of alkyl substitution appears to have an influence on the reactivity and formation of substituted allyl systems. For example, terminally disubstituted allylpotassiums such as those derived from olefins **21**, **25**, and **26** show a tendency to undergo ethylene insertion reactions. The pattern of alkyl substitution of may also be of importance in cases where different allylpotassiums can be derived from the same olefin by competing metalation at different positions, as in the cases of olefins **28–32**.

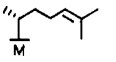
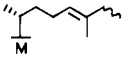
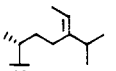
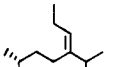
These generalizations are intended as "rules of thumb" in the synthetic application of this reaction and are listed roughly in order of their importance. Clearly a more thorough study, beyond the scope of the present work, of the magnitudes of these effects, especially of the steric and electronic factors involved in the metalation of olefins having competing sites for deprotonation, is needed to provide a more complete knowledge of this highly useful reaction.

In an effort to control the regioselectivity of the reaction, metal salts were added to the allylpotassium obtained from 2-ethyl-3-methyl-1-butene (**18**) (Figure 4). Whereas the allylpotassium itself yields a mixture of fucosterol *i*-methyl ether (**23**) and branched isomer (**24**) (64%/36%), a modest reversal of regioselectivity (48%/52%) was observed after conversion to the allyl Grignard by addition of 1 molar equiv of magnesium bromide. Addition of cerium chloride[25] did not lead to reaction with iodide **1**. On the other hand, addition of $^1/_4$ molar equiv of Li_2CuCl_3[26] led to pure fucosterol *i*-methyl ether,[27] with complete suppression of the minor, branched, regioisomer **34**. This new regiocontrol method was extended to the synthesis of the *i*-methyl ethers of desmosterol (**37**) and 24(*E*)-propylidenecholesterol (**35**)[28] with good results (Table IV). Most remarkably, the preferred endo conformation of the allylpotassium was maintained upon addition of the copper salt.

Summary

Allyl organometallics prepared directly from the corresponding olefins provide an extremely straightforward route to Δ^{24} and $\Delta^{24(28)}$ sterols compared to most literature methods.[29] The convenience of this method is enhanced by the ready availability of iodide **1** from stigmasterol (five steps in 41% yield)[4] and the stability of this crystalline solid under ordinary conditions. Tentative rules of thumb were drawn concerning the use of the metalation reaction for stereodefined product formation. Side reactions due to ethylene insertion in the cases of terminally disubstituted anions may lead to preparatively useful methods. An unprecedented regiochemical control in favor of the less substituted terminus of the allyl system has been accomplished by addition of Li_2CuCl_3. This allowed the high-yield synthesis of biosynthetically important sterols such as fucosterol (**33**) and desmosterol (**37**).

Table IV. Synthesis of Sterol Side Chains via Cu^I-Modified Reaction of Allylpotassiums

olefin	product	yield, %
 **21**	 **37**	69
 **25**	 **48,49**	53 (*E*/*Z* 3:1)
 **18**	 **33**	65
 **19**	 **35**	54

Experimental Section

General Methods. High-pressure liquid chromatography (HPLC) was carried out on a Waters Associates HPLC system (M 6000 pump, R403 differential refractometer) with two Altex Ultrasphere ODS 5-μm columns (10 mm i.d. × 25 cm) in series with either methanol (MeOH) or acetonitrile–methanol–ethyl acetate, 3:1:1 (MeCN/MeOH/EtOAc), as the mobile phase (3 mL/min). Low-resolution mass spectra were obtained with either a Finnigan MAT-44 spectrometer; a Hewlett-Packard GC/MS system consisting of a Model 5890A gas chromatograph with a SE-54 coated fused silica capillary column (0.32 mm i.d. × 15 m), a model 5970 mass spectrometer, and a 9133 system for data acquisition; or a Hewlett-Packard Model 5995 GC/MS in the direct inlet mode. Melting points were determined on a Thomas-Hoover Unimelt capillary melting point apparatus and are uncorrected. Nuclear magnetic resonance spectra (NMR) were recorded on a Varian XL-400 instrument. All NMR spectra are referenced to the solvent peak ($CHCl_3$). All reagents were obtained commercially, with the exception of **1**,[4] **4**, **9**, **19**, **20**, and **69**,[13] and were used without further purification. High-resolution ^{1}H NMR spectra of all new compounds described in this article that show the absence of contaminants were submitted for inspection prior to acceptance.

General Method for Allylpotassium Reaction. To 10 mL of dry THF at −78 °C under Ar was added 3.2 mL of 1.6 M *n*-BuLi/hexane (5.1 mmol). After 5 min, 0.60 g of KOt-Bu (5.4 mmol) was added, and the mixture was stirred 5 min at −78 °C. Olefin (1.0 mL, 14-6 mmol) was added, and the temperature was raised to −55 °C. Alternatively the olefin could be added first, then the *n*-BuLi and KOt-Bu. After 1 h the temperature had typically risen to −48 °C. The yellow or orange solution was then cooled to −78 °C, and a solution of the iodide **1**[4] in 3 mL of THF was added. Amounts of **1** varying from 50 mg to 1 g (0.11–2.19 mmol) were used with consistent results. Thus, when the allylpotassium derived from 2-methyl-2-pentene (**22**) was reacted

(24) (a) Schlosser, M.; Rauchschwalbe, G. *J. Am. Chem. Soc.* **1978**, *100*, 3258–3260. (b) Bosshardt, H.; Schlosser, M. *Helv. Chim. Acta* **1980**, *63*, 2393–2403.

(25) Guo, B.-S.; Doubleday, W.; Cohen, T. *J. Am. Chem. Soc.* **1987**, *109*, 4710–4711.

(26) Malik, W. U.; Tyagi, J. S. *Indian J. Chem., Sect. A* **1981**, *20A*, 1208–1209.

(27) Sucrow, W.; Raduechel, B. *Chem. Ber.* **1970**, *103*, 2711–2717.

(28) Rohmer, M.; Kokke, W. C. M. C.; Fenical, W.; Djerassi, C. *Steroids* **1980**, *35*, 219–231.

(29) Piatak, D. M.; Wicha, J. *Chem. Rev.* **1978**, *78*, 199–241.

with 1 g of 1, the same yield and product ratio was obtained as when only 47 mg of 1 was used. After 5 min the reaction mixture was poured into water and extracted with ether. The ether layer was dried over Na_2SO_4 and evaporated to dryness. The crude product was purified by silica gel column chromatography (eluent: hexanes followed by hexanes/ether, 79:1) or by preparative TLC (eluent: hexanes/ether, 39:1). Analysis was carried out by HPLC separation and NMR spectroscopy of the deprotected sterols. Deprotection consisted of hydrolysis of the *i*-methyl ether by heating with 0.05% *p*-toluenesulfonic acid in refluxing dioxane-/water, 9:1, under reflux for 1.5 h. The composition of a mixture was determined by integration of the HPLC trace or, if the HPLC separation was not good enough, integration of the olefinic region of the ^1H NMR spectrum of the mixture. Sterols **57a** and **57b** could not be completely separated. Sterols **66** and **68** were not purified and are characterized only by the olefinic region of the NMR spectra. Sterol **65** has been previously isolated from a marine sponge.[30] Both isomers of sterols **34**, **36**, **42**, **46**, **50**, **58**, **60**, **63**, and **48** were separated and characterized as the Δ^5 sterols. Both isomers of steroid **75** were separated and characterized as the *i*-methyl ethers. No stereochemical assignments were made for these compounds (see Tables I and II for products and yields).

General Method for Cuprous Salt Modification of the Allylpotassium Reaction. To the allylpotassium prepared as above at −78 °C was added 1.25 mL of a 1 M solution of Li_2CuCl_3[26] in THF (prepared from 516 mg of CuCl (5.2 mmol) and 452 mg of LiCl (10.6 mmol) in 5 mL of dry THF). The clear orange solution immediately became black. Upon shaking, it quickly lightened to a tan color and had a gelatinous consistency. A solution of 1 (300–500 mg, 0.66–1.10 mmol) in 3 mL of THF was introduced, and the temperature was raised to −35 °C and allowed to warm slowly. After 2.5 h (final temperature = −15 °C) the reactions with the olefins **21** and **25** were complete. The reactions with **18** and **19** were slower, requiring 16 h (final temperature = 10 °C) and 25 h (final temperature = 15 °C) respectively for completion. During the course of the reaction the mixture became black and less viscous. The reaction was poured into water and extracted with ether. Filtration of the extraction mixture improved the separation of the phases. Purification and analysis were carried out as described above (see Table III for products and yields). Typically 15% of the reaction products was due to reduction of the iodide to the steroid hydrocarbon side chain (**70**).[16] When more than $^1/_4$ molar equiv of Cu^I was used, **70** was the major products. See Table IV for products and yields.

Allylpotassium Reaction of 2,3-Dimethyl-2-butene (26) in THF-d_8. The allylpotassium of **26** was prepared in 7 mL of perdeuterated THF as described above. Reaction with 64.7 mg of 1 (0.14 mmol) and hydrolysis of the *i*-methyl ether gave the following sterols after HPLC: **70-N** (4%), **46-N** (1%), **45-N** (2%), **3-N** (25%), **52-N** (14%), **51-N** (48%), and **12-N** (3%). Only **12-N** showed deuterium incorporation by mass spectrometry to the extent of four deuteriums.

Allylpotassium Reaction of 2,3-Dimethylbutadiene (76). To a solution of 0.85 mL of 2,2,6,6-tetramethylpiperidine (5.1 mmol) and 10 mL of THF at −78 °C under Ar was added 3.2 mL of 1.6 M *n*-BuLi/hexane (5.1 mmol) and 0.60 g of KOt-Bu (5.4 mmol).[20] The mixture was warmed to −50 °C and stirred for 15 min until the KOt-Bu was dissolved. After cooling to −78 °C 1 mL of the diene **76** (9.75 mmol) was added. The mixture immediately turned deep red. After 45 min at −78 °C, 115 mg 1 (0.25 mmol) in 1 mL of THF was added. After 15 min the reaction was worked up as described above to give 96 mg of ergosta-5,24(28),25-trien-3β-ol *i*-methyl ether **77-M** (93%).[21]

Birch Reduction of 6β-Methoxy-3α,5-cycloergosta-24(28),25-diene (77-M). To a solution of 50 mg of Li in 10 mL of NH_3 was added 54 mg of **77** in 1 mL of Et_2O. After 2 h 5 mL of EtOH/Et_2O, 1:1, was added and the NH_3 allowed to evaporate. Extraction with water and ether followed by the workup described above gave 43 mg of **51-M** (80%).[19]

(20*S*)-21-Iodo-20-methylpregn-7-en-3β-ol Tetrahydropyranyl Ether (4). 5,6-Dihydroergosterol tetrahydropyranyl ether was selectively ozonized to the protected 20-methylpregn-7-ene-3β,21-diol.[31] Conversion to the tosylate and treatment with sodium iodide[4] gave the iodide: mp 132–134 °C (acetone); ^1H NMR (400 MHz) δ ($CDCl_3$) 5.151 (m, 1 H, C7), 4.727 (m, 1 H, THP), 3.922 (m, 1 H, THP), 3.595 (m, 1 H, C3), 3.485 (m, 1 H, THP), 3.331 (dd, *J* = 9.5, 2.6 Hz, 1 H, C21), 3.167 (dd, *J* = 9.5, 5.6 Hz, 1 H, C21), 1.031 (d, *J* = 6.1 Hz, 3 H, C20 methyl), 0.787 (s, 3 H, C19), 0.563 (s, 3 H, C18); low-resolution mass spectrum, *m/z* (relative intensity) 526 (M^+, $C_{27}H_{43}IO_2$, 16), 425 (28), 424 (22), 105 (10), 95 (12), 91 (14), 85 (100), 67 (22), 55 (23).

2,3-Dimethyl-3-ethyl-1-pentene (9).[32] A mixture of 2 g of $NaNH_2$ (50 mmol) and 18 g of methyl triphenylphosphonium bromide (50 mmol) in 75 mL of dry ether was heated under reflux for 4 h in an Ar atmosphere. 3-Ethyl-3-methyl-2-pentanone (5.4 g, 42 mmol) was added, and heating under reflux continued overnight. Acetone was added to quench the Wittig reagent; the mixture was filtered and fractionally distilled. After removal of the solvent, biphenyl (7 g) was added and the distillation was continued. The product distilled at 131 °C (3.6 g, 66%): ^1H NMR (400 MHz) δ ($CDCl_3$) 4.835 (s, 1 H, C1), 4.643 (s, 1 H, C1), 1.625 (s, 3 H, 2-methyl), 1.440 (sext, *J* = 7.3 Hz, 2 H, C4), 1.237 (sext, *J* = 7.3 Hz, 2 H, C4), 0.937 (s, 3 H, 3-methyl), 0.712 (t, *J* = 7.4 Hz, 6 H, C5).

2-(1-Methylethyl)-1-pentene (19).[33] The above procedure was used starting from 2-methyl-3-hexanone: ^1H NMR (400 MHz) δ ($CDCl_3$) 4.735 (s, 1 H, C1), 4.669 (s, 1 H, C1), 2.226 (sept, *J* = 6.7 Hz, 1 H, i-Pr methine), 1.999 (t, *J* = 7.6 Hz, 2 H, C3), 1.459 (sext, *J* = 7.5 Hz, 2 H, C4), 1.026 (d, *J* = 6.8 Hz, 6 H, i-Pr methyls), 0.913 (t, *J* = 7.3 Hz, 3 H, C5).

2,3-Dimethyl-3-hexene (20).[34] The above procedure with the substitution of propyl triphenylphosphonium bromide and 3-methyl-2-butanone was used giving a mixture of the following isomers.

2,3-Dimethyl-3(*E*)-hexene (30%): ^1H NMR (400 MHz) δ ($CDCl_3$) 5.125 (t, *J* = 6.6 Hz, 1 H, C4), 2.204 (sept, *J* = 6.8 Hz, 1 H, C2), 1.995 (quint, *J* = 7.6 Hz, 2 H, C5), 1.553 (s, 3 H, 3-methyl), 0.979 (d, *J* = 7.2 Hz, 6 H, C1), 0.935 (t, *J* = 7.5 Hz, 3 H, C6).

2,3-Dimethyl-3(*Z*)-hexene (70%): ^1H NMR (400 MHz) δ ($CDCl_3$) 5.044 (t, *J* = 7.0 Hz, 1 H, C4), 2.805 (sept, *J* = 6.9, 1 H, C2), 1.995 (quint, *J* = 7.6 Hz, 2 H, C5), 1.588 (s, 3 H, 3-methyl), 0.957 (d, *J* = 7.0 Hz, 6 H, C1), 0.935 (t, *J* = 7.5 Hz, 3 H, C6).

26,27-Dinorergosta-5,24-dien-3β-ol (16-N):[10] mp 132–134 °C (MeOH); HPLC t_R 40.5 min (MeOH); ^1H NMR (400 MHz) δ ($CDCl_3$) 5.351 (m, 1 H, C6), 4.668 (s, 1 H, C25), 4.655 (s, 1 H, C25), 1.708 (s, 3 H, C28), 1.004 (s, 3 H, C19), 0.932 (d, *J* = 6.5 Hz, 3 H, C21), 0.677 (s, 3 H, C18); low-resolution mass spectrum, *m/z* (relative intensity) 370 (M^+, $C_{26}H_{42}O$, 8), 355 (11), 314 (43), 271 (51), 213 (22), 145 (38), 91 (58), 81 (71), 55 (100).

23-Methylergosta-5,24(28)-dien-3β-ol A (34a-N): mp 135–137 °C (MeOH); HPLC t_R 58 min (MeOH); ^1H NMR (400 MHz) δ ($CDCl_3$) 5.349 (m, 1 H, C6), 4.783 (s, 1 H, C28), 4.707 (s, 1 H, C28), 1.041 (d, *J* = 6.9 Hz, 3 H, C26), 1.019 (d, *J* = 6.9 Hz, 3 H, C27), 1.002 (s, 3 H, C19), 0.994 (d, *J* = 6.7 Hz, 3 H, 23-methyl), 0.898 (d, *J* = 6.4 Hz, C21), 0.642 (s, 3 H, C18); low-resolution mass spectrum, *m/z* (relative intensity) 412 (M^+, $C_{29}H_{48}O$, 2), 314 (67), 299 (11), 281 (17), 229 (26), 213 (16), 211 (16), 83 (48), 69 (61), 55 (100).

23-Methylergosta-5,24(28)-dien-3β-ol B (34b-N): mp 147–150 °C (MeOH); HPLC t_R 59 min (MeOH); ^1H NMR (400 MHz) δ ($CDCl_3$) 5.349 (m, 1 H, C6), 4.726 (s, 1 H, C28), 4.687 (s, 1 H, C28), 1.032 (d, *J* = 6.7 Hz, 3 H, C26), 1.020 (d, *J* = 6.7 Hz, 3 H, C27), 1.011 (s, 3 H, C19), 0.972 (d, *J* = 6.7 Hz, 3 H, 23-methyl), 0.924 (d, *J* = 6.7 Hz, 3 H, C21), 0.703 (s, 3 H, C18); low-resolution mass spectrum, *m/z* (relative intensity) 412 (M^+, $C_{29}H_{48}O$, 1), 314 (36), 300 (19), 281 (12), 229 (17), 213 (13), 211 (11), 69 (67), 55 (100).

23-Ethylergosta-5,24(28)-dien-3β-ol A (36a-N): mp 129–131 °C (MeOH); HPLC t_R 68.5 min (MeOH), 79 min (MeCN/MeOH/EtOAc); ^1H NMR (400 MHz) δ ($CDCl_3$) 5.349 (m, 1 H,

(30) Li, X.; Djerassi, C. *Tetrahedron Lett.* **1983**, *24*, 665–668.

(31) Moreau, J. P.; Aberhart, D. J.; Caspi, E. *J. Org. Chem.* **1974**, *39*, 2018–2023.

(32) Sun, S.; Long, Y. *Huanjing Haxue* **1982**, *1*, 443–449; *Chem. Abstr.* **1983**, *99*, 58555*v*.

(33) McLain, S. J.; Sancho, J.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 5451–5453.

(34) Barluenga, J.; Yus, M.; Concellón, J. M.; Bernad, P. *J. Org. Chem.* **1983**, *48*, 3116–3118.

C6), 4.835 (s, 1 H, C28), 4.695 (s, 1 H, C28), 1.045 (d, J = 6.7 Hz, 3 H, C26), 1.014 (d, J = 6.7 Hz, 3 H, C27), 1.002 (s, 3 H, C19), 0.893 (d, J = 6.3 Hz, 3 H, C21), 0.836 (t, J = 7.3 Hz, 3 H, CH_2CH_3), 0.641 (s, 3 H, C18); low-resolution mass spectrum, m/z (relative intensity) 426 (M^+, $C_{30}H_{50}O$, 2), 314 (37), 300 (13), 281 (21), 229 (18), 213 (11), 211 (11), 112 (52), 83 (48), 69 (100), 55 (92).

23-Ethylergosta-5,24(28)-dien-3β-ol B (36b-N): mp 123–125 °C (MeOH); HPLC t_R 68.5 min (MeOH), 78 min (MeCN/MeOH/EtOAc); ^1H NMR (400 MHz) δ ($CDCl_3$) 5.349 (m, 1 H, C6), 4.790 (s, 1 H, C28), 4.658 (s, 1 H, C28), 1.028 (d, J = 6.7 Hz, 3 H, C26), 1.018 (d, J = 6.7 Hz, 3 H, C27), 1.008 (s, 3 H, C19), 0.921 (d, J = 6.7 Hz, 3 H, C21), 0.794 (t, J = 7.4 Hz, 3 H, CH_2CH_3), 0.695 (s, 3 H, C18); low-resolution mass spectrum, m/z (relative intensity) 426 (M^+, $C_{30}H_{50}O$, 2), 314 (43), 281 (12), 229 (20), 213 (12), 211 (13), 112 (68), 83 (58), 69 (100), 55 (95).

23,23-Dimethyl-26,27-dinorcholesta-7,24-dien-3β-ol (40-L): mp 165–167 °C (MeOH); HPLC t_R 42 min (MeOH); ^1H NMR (400 MHz) δ ($CDCl_3$) 5.801 (dd, J = 17.6, 10.3 Hz, 1 H, C24), 5.155 (m, 1 H, C7), 4.875 (d, J = 17.6 Hz, 1 H, C25), 4.870 (d, J = 10.3 Hz, 1 H, C25), 0.986 (s, 3 H, 23-methyl), 0.979 (s, 3 H, 23-methyl), 0.936 (d, J = 6.5 Hz, 3 H, C21), 0.788 (s, 3 H, C19), 0.535 (s, 3 H, C18); low-resolution mass spectrum, m/z (relative intensity) 384 (M^+, $C_{28}H_{44}O$, 95), 369 (37), 300 (12), 271 (100), 255 (34), 231 (23), 213 (27), 69 (63).

26-Methyl-27-norergosta-5,24(Z)-dien-3β-ol (41-N): mp 119–121 °C (MeOH); HPLC t_R 55.5 min (MeOH); ^1H NMR (400 MHz) δ ($CDCl_3$) 5.351 (m, 1 H, C6), 5.090 (d, J = 6.9 Hz, 1 H, C25), 1.660 (s, 3 H, C28), 1.008 (s, 3 H, C19), 0.959 (d, J = 6.4 Hz, 3 H, C21), 0.933 (t, J = 7.6 Hz, 3 H, CH_2CH_3), 0.682 (s, 3 H, C18); low-resolution mass spectrum, m/z (relative intensity) 398 (M^+, $C_{28}H_{46}O$, 17), 314 (100), 299 (39), 281 (25), 271 (24), 229 (25), 55 (38).

23-Ethyl-26,27-dinorergosta-5,24-dien-3β-ol A (42a-N): mp 165–166 °C (MeOH); HPLC t_R 50 min (MeOH); ^1H NMR (400 MHz) δ ($CDCl_3$) 5.351 (m, 1 H, C6), 4.742 (s, 1 H, C25), 4.662 (s, 1 H, C25), 1.551 (s, 3 H, C28), 1.003 (s, 3 H, C19), 0.881 (d, J = 6.4 Hz, 3 H, C21), 0.797 (t, J = 7.4 Hz, 3 H, cH_2CH_3), 0.656 (s, 3 H, C18); low-resolution mass spectrum, m/z (relative intensity) 398 (M^+, $C_{28}H_{46}O$, 5), 314 (100), 299 (13), 281 (21), 271 (11), 229 (20), 213 (10), 55 (16).

23-Ethyl-26,27-dinorergosta-5,24-dien-3β-ol B (42b-N): mp 167–169 °C (MeOH); HPLC t_R 53 min (MeOH); ^1H NMR (400 MHz) δ ($CDCl_3$) 5.351 (m, 1 H, C6), 4.696 (s, 1 H, C25), 4.664 (s, 1 H, C25), 1.611 (s, 3 H, C28), 1.008 (s, 3 H, C19), 0.917 (d, J = 6.6 Hz, 3 H, C21), 0.773 (t, J = 7.4 Hz, 3 H, CH_2CH_3), 0.691 (s, 3 H, C18); low-resolution mass spectrum, m/z (relative intensity) 398 (M^+, $C_{28}H_{46}O$, 11), 314 (100), 300 (56), 281 (22), 271 (28), 229 (17), 55 (42).

26-Ethylcholesta-5,25(Z)-dien-3β-ol (43-N): mp 88–90 °C (MeOH); HPLC t_R 56 min (MeOH); ^1H NMR (400 MHz) δ ($CDCl_3$) 5.351 (m, 1 H, C6), 5.111 (t, J = 7.0 Hz, 1 H, C26), 1.664 (d, J = 1.2 Hz, 3 H, C27), 1.006 (s, 3 H, C19), 0.928 (t, J = 7.5 Hz, 3 H, CH_2CH_3), 0.917 (d, J = 6.6 Hz, 3 H, C21), 0.677 (s, 3 H, C18); low-resolution mass spectrum, m/z (relative intensity) 412 (M^+, $C_{29}H_{48}O$, 100), 397 (19), 394 (12), 379 (18), 299 (52), 271 (87), 255 (30), 213 (47), 145 (50), 105 (51), 69 (46), 55 (82).

27-Norcholesta-5,24(E)-dien-3β-ol (45-N): mp 121–123 °C (MeOH); HPLC t_R 44 min (MeOH); ^1H NMR (400 MHz) δ ($CDCl_3$) 5.398 (m, 2 H, C24, C25), 5.353 (m, 1 H, C6), 1.636 (d, J = 4.4 Hz, 3 H, C26), 1.006 (s, 3 H, C19), 0.914 (d, J = 6.6 Hz, 3 H, C21), 0.674 (s, 3 H, C18); low-resolution mass spectrum, m/z (relative intensity) 370 (M^+, $C_{26}H_{42}O$, 7), 355 (27), 352 (7), 337 (13), 300 (17), 271 (77), 213 (20), 55 (100).

23-Methyl-26,27-dinorcholesta-5,24-dien-3β-ol A (46a-N): mp 160–162 °C (MeOH); HPLC t_R 37 min (MeOH); ^1H NMR (400 MHz) δ ($CDCl_3$) 5.566 (ddd, J = 17.2, 10.2, 8.4 Hz, 1 H, C24), 5.351 (m, 1 H, C6), 4.940 (d, J = 17.2 Hz, 1 H, C25), 4.904 (d, J = 10.2 Hz, 1 H, C25), 1.004 (s, 3 H, C19), 0.962 (d, J = 6.7 Hz, 3 H, 23-methyl), 0.893 (d, J = 6.5 Hz, 3 H, C21), 0.665 (s, 3 H, C18); low-resolution mass spectrum, m/z (relative intensity) 370 (M^+, $C_{26}H_{42}O$, 45), 355 (16), 352 (24), 337 (53), 300 (34), 285 (31), 271 (20), 213 (33), 55 (100).

23-Methyl-26,27-dinorcholesta-5,24-dien-3β-ol B (46b-N): mp 146–148 °C (MeOH); HPLC t_R 41 min (MeOH); ^1H NMR (400 MHz) δ ($CDCl_3$) 5.770 (ddd, J = 17.0, 10.3, 6.9 Hz, 1 H, C24), 5.351 (m, 1 H, C6), 4.942 (d, J = 17.0 Hz, 1 H, C25), 4.861 (d, J = 10.3 Hz, 1 H, C25), 1.009 (s, 3 H, C19), 0.927 (d, J = 6.7 Hz, 3 H, 23-methyl), 0.916 (d, J = 6.5 Hz, 3 H, C21), 0.696 (s, 3 H, C18); low-resolution mass spectrum, m/z (relative intensity) 370 (M^+, $C_{26}H_{42}O$, 17), 355 (8), 352 (14), 337 (14), 300 (25), 285 (66), 271 (27), 213 (23), 55 (100).

27-Norcholesta-5,24(Z)-dien-3β-ol (47-N):[10] mp 126–129 °C (MeOH); HPLC t_R 44 min (MeOH); ^1H NMR (400 MHz) δ ($CDCl_3$) 5.398 (br m, 2 H, C24, C25), 5.353 (m, 1 H, C6), 1.605 (d, J = 6.2 Hz, 3 H, C26), 1.008 (s, 3 H, C19), 0.945 (d, J = 6.6 Hz, 3 H, C21), 0.680 (s, 3 H, C18); low-resolution mass spectrum, m/z (relative intensity) 370 (M^+, $C_{26}H_{42}O$, 14), 355 (35), 352 (12), 337 (20), 300 (22), 271 (100), 213 (27), 55 (100).

25-Ethyl-27-norcholesta-5,24(E)-dien-3β-ol (48-N): mp 116–117 °C (MeOH); HPLC t_R 47 min (MeOH), 51 min (MeCN/MeOH/EtOAc); ^1H NMR (400 MHz) δ ($CDCl_3$) 5.351 (m, 1 H, C6), 5.087 (t, J = 7.0 Hz, 1 H, C24), 1.596 (s, 3 H, C27), 1.008 (s, 3 H, C19), 0.978 (t, J = 7.5 Hz, 3 H, CH_2CH_3), 0.939 (d, J = 6.6 Hz, 3 H, C21), 0.677 (s, 3 H, C18); low-resolution mass spectrum, m/z (relative intensity) 398 (M^+, $C_{28}H_{46}O$, 3), 383 (2), 365 (1), 300 (8), 271 (33), 213 (11), 145 (84), 133 (39), 119 (39), 107 (43), 105 (56), 55 (100).

25-Ethyl-27-norcholesta-5,24(Z)-dien-3β-ol (49-N): mp 117–118 °C (MeOH); HPLC t_R 47 min (MeOH), 48 min (MeCN/MeOH/EtOAc); ^1H NMR (400 MHz) δ ($CDCl_3$) 5.351 (m, 1 H, C6), 5.062 (t, J = 6.9 Hz, 1 H, C24), 1.673 (s, 3 H, C27), 1.008 (s, 3 H, C19), 0.963 (t, J = 7.5 Hz, 3 H, CH_2CH_3), 0.934 (d, J = 6.6 Hz, 3 H, C21), 0.678 (s, 3 H, C18); low-resolution mass spectrum, m/z (relative intensity) 398 (M^+, $C_{28}H_{46}O$, 4), 383 (3), 365 (2), 300 (11), 271 (46), 213 (16), 145 (84), 133 (72), 119 (79), 107 (90), 105 (100), 55 (72).

23-Ethyl-23-methyl-26,27-dinorcholesta-5,24-dien-3β-ol A (50a-N): mp 147–152 °C (MeOH); HPLC t_R 47.5 min (MeOH), 49 min (MeCN/MeOH/EtOAc); ^1H NMR (400 MHz) δ ($CDCl_3$) 5.651 (dd, J = 17.6, 10.8 Hz, 1 H, C24), 5.351 (m, 1 H, C6), 4.970 (d, J = 10.8 Hz, 1 H, C25), 4.861 (d, J = 17.6 Hz, 1 H, C25), 1.001 (s, 3 H, C19), 0.946 (d, J = 6.6 Hz, 3 H, C21), 0.937 (s, 3 H, 23-Me), 0.763 (t, J = 7.4 Hz, 3 H, CH_2CH_3), 0.669 (s, 3 H, C18); low-resolution mass spectrum, m/z (relative intensity) 398 (M^+, $C_{28}H_{46}O$, 2), 314 (10), 299 (6), 271 (25), 213 (21), 159 (55), 145 (52), 55 (100).

23-Ethyl-23-methyl-26,27-dinorcholesta-5,24-dien-3β-ol B (50b-N): mp 167–170 °C (MeOH); HPLC t_R 50 min (MeOH); ^1H NMR (400 MHz) δ ($CDCl_3$) 5.713 (dd, J = 17.6, 10.8 Hz, 1 H, C24), 5.351 (m, 1 H, C6), 4.946 (d, J = 10.8 Hz, 1 H, C25), 4.842 (d, J = 17.6 Hz, 1 H, C25), 1.002 (s, 3 H, C19), 0.933 (s, 3 H, 23-Me), 0.913 (d, J = 6.4 Hz, 3 H, C21), 0.754 (t, J = 7.4 Hz, 3 H, CH_2CH_3), 0.683 (s, 3 H, C18); low-resolution mass spectrum, m/z (relative intensity) 398 (M^+, $C_{28}H_{46}O$, 5), 383 (4), 369 (6), 314 (10), 299 (6), 271 (36), 213 (25), 159 (52), 145 (61), 55 (100).

23,23-Dimethyl-26,27-dinorergosta-5,24-dien-3β-ol (52-N): mp 170–172 °C (MeOH); HPLC t_R 55 min (MeOH); ^1H NMR (400 MHz) δ ($CDCl_3$) 5.352 (m, 1 H, C6), 4.712 (s, 2 H, C25), 1.724 (s, 3 H, C28), 1.044 (s, 3 H, 23-methyl), 1.009 (s, 3 H, C19), 1.002 (s, 3 H, 23-methyl), 0.904 (d, J = 6.4 Hz, 3 H, C21), 0.681 (s, 3 H, C18); low-resolution mass spectrum, m/z (relative intensity) 398 (M^+, $C_{28}H_{46}O$, 1), 314 (13), 271 (16), 84 (100), 55 (47).

25-(2-Propylidene)-27-norcholest-5-en-3β-ol (53-N): mp 125–126 °C (MeOH); HPLC t_R 52 min (MeOH); ^1H NMR (400 MHz) δ ($CDCl_3$) 5.351 (m, 1 H, C6), 1.633 (s, 9 H, C26 and C-$(CH_3)_2$), 1.004 (s, 3 H, C19), 0.913 (d, J = 6.6 Hz, 3 H, C21), 0.672 (s, 3 H, C18); low-resolution mass spectrum, m/z (relative intensity) 412 (M^+, $C_{29}H_{48}O$, 57), 397 (5), 379 (5), 299 (7), 271 (18), 213 (10), 145 (20), 83 (79), 55 (100).

24-Methylergosta-5,25-dien-3β-ol (54-N): mp 147–149 °C (MeOH); HPLC t_R 51 min (MeOH); ^1H NMR (400 MHz) δ ($CDCl_3$) 5.351 (m, 1 H, C6), 4.713 and 4.648 (s, 1 H, C26), 1.678 (s, 3 H, C27), 1.003 (s, 9 H, C19 and C24 methyls), 0.904 (d, J = 6.6 Hz, 3 H, C21), 0.663 (s, 3 H, C18); low-resolution mass spectrum, m/z (relative intensity) 412 (M^+, $C_{29}H_{48}O$, 100), 397 (11), 328 (86), 299 (25), 271 (34), 213 (18), 145 (21), 84 (39), 69 (34), 55 (49).

25-Vinyl-27-norcholesta-5,24(Z)-dien-3β-ol (55-N): mp 109–112 °C (MeOH); HPLC t_R 41.5 min (MeOH); ^1H NMR (400 MHz) δ ($CDCl_3$) 6.366 (dd, J = 17.4, 10.7 Hz, 1 H, $CHCH_2$), 5.469 (t, J = 7.1 Hz, 1 H, C24), 5.353 (m, 1 H, C6), 5.066 (d, J = 17.4 Hz, 1 H, $CHCH_2$), 4.911 (d, J = 10.9 Hz, 1 H, $CHCH_2$), 1.734 (s,

3 H, C26), 1.007 (s, 3 H, C19), 0.950 (d, J = 6.4 Hz, 3 H, C21), 0.678 (s, 3 H, C18); low-resolution mass spectrum, m/z (relative intensity) 396 (M^+, $C_{28}H_{44}O$, 2), 363 (1), 299 (2), 253 (8), 105 (34), 95 (38), 93 (28), 91 (35), 81 (100), 79 (62), 67 (44), 55 (62).

23,23-Divinylcholest-5-en-3β-ol (56-N): mp 155–157 °C (MeOH); HPLC t_R 39 min (MeOH); ^{1}H NMR (400 MHz) δ ($CDCl_3$) 5.857 (dd, J = 17.4, 10.7 Hz, 1 H, CHCH$_2$), 5.822 (dd, J = 17.4, 10.7 Hz, 1 H, CHCH$_2$), 5.349 (m, 1 H, C6), 4.961 (d, J = 10.7 Hz, 1 H, CHCH_2), 4.930 (d, J = 17.5 Hz, 1 H, CHCH_2), 1.105 (s, 3 H, C24), 1.001 (s, 3 H, C19), 0.946 (d, J = 6.5 Hz, 3 H, C21), 0.677 (s, 3 H, C18); low-resolution mass spectrum, m/z (relative intensity) 396 (M^+, $C_{28}H_{44}O$, 27), 381 (13), 367 (8), 315 (11), 297 (50), 271 (100), 213 (18), 159 (28), 133 (31), 81 (99), 79 (51), 67 (39), 55 (41).

27-Norergosta-5,24(*Z*)-dien-3β-ol (57a-N):[10] HPLC t_R 47 min (MeOH), 50 min (MeCN/MeOH/EtOAc); ^{1}H NMR (400 MHz) δ ($CDCl_3$) 5.351 (m, 1 H, C6), 5.187 (q, J = 6.4 Hz, 1 H, C25), 1.579 (s, 3 H, C28), 1.008 (s, 3 H, C19), 0.924 (d, J = 6.6 Hz, 3 H, C21), 0.674 (s, 3 H, C18).

27-Norergosta-5,24(*E*)-dien-3β-ol (57b-N):[10] mp 121–123 °C (MeOH); HPLC t_R 47 min (MeOH), 49 min (MeCN/MeOH/EtOAc); ^{1}H NMR (400 MHz) δ ($CDCl_3$) 5.351 (m, 1 H, C6), 5.170 (q, J = 6.4 Hz, 1 H, C25), 1.661 (s, 3 H, C28), 1.008 (s, 3 H, C19), 0.966 (d, J = 6.6 Hz, 3 H, C21), 0.683 (s, 3 H, C18).

23-Methyl-26,27-dinorergosta-5,24-dien-3β-ol A (58a-N): mp 166–168 °C (MeOH); HPLC t_R 40 min (MeOH); ^{1}H NMR (400 MHz) δ ($CDCl_3$) 5.354 (m, 1 H, C6), 4.678 (s, 2 H, C25), 1.608 (s, 3 H, C28), 1.004 (s, 3 H, C19), 0.970 (d, J = 6.8 Hz, 3 H, 23-methyl), 0.889 (d, J = 6.4 Hz, 3 H, C21), 0.657 (s, 3 H, C18); low-resolution mass spectrum, m/z (relative intensity) 384 (M^+, $C_{27}H_{44}O$, 7), 314 (100), 300 (17), 299 (16), 271 (30), 229 (26), 213 (24), 105 (63), 69 (68), 55 (75).

23-Methyl-26,27-dinorergosta-5,24-dien-3β-ol B (58b-N): mp 149–151 °C (MeOH); HPLC t_R 43.5 min (MeOH); ^{1}H NMR (400 MHz) δ ($CDCl_3$) 5.354 (m, 1 H, C6), 4.670 (s, 1 H, C25), 4.640 (s, 1 H, C25), 1.690 (s, 3 H, C28), 1.010 (s, 3 H, C19), 0.954 (d, J = 6.7 Hz, 3 H, 23-methyl), 0.918 (d, J = 6.5 Hz, 3 H, C21), 0.699 (s, 3 H, C18); low-resolution mass spectrum, m/z (relative intensity) 384 (M^+, $C_{27}H_{44}O$, 9), 314 (100), 300 (78), 299 (29), 271 (58), 229 (26), 213 (22), 105 (25), 69 (31), 55 (29).

27-Norstigmasta-5,24(*E*)-dien-3β-ol (59-N): mp 124–125 °C (MeOH); HPLC t_R 47.5 min (MeOH), 47 min (MeCN/MeOH/EtOAc); ^{1}H NMR (400 MHz) δ ($CDCl_3$) 5.351 (m, 1 H, C6), 5.149 (q, J = 6.7 Hz, 1 H, C25), 1.571 (d, J = 6.7 Hz, 3 H, C26), 1.008 (s, 3 H, C19), 0.949 (t, J = 7.6 Hz, 3 H, C29), 0.932 (d, J = 6.6 Hz, 3 H, C21), 0.677 (s, 3 H, C18); low-resolution mass spectrum, m/z (relative intensity) 398 (M^+, $C_{28}H_{46}O$, 9), 383 (4), 314 (77), 299 (32), 281 (30), 271 (42), 229 (57), 213 (40), 161 (46), 145 (100), 105 (63).

23-Methyl-27-norergosta-5,24(28)-dien-3β-ol A (60a-N): mp 150–152 °C (MeOH); HPLC t_R 42 min (MeOH); ^{1}H NMR (400 MHz) δ ($CDCl_3$) 5.351 (m, 1 H, C6), 4.730 (s, 1 H, C28), 4.709 (s, 1 H, C28), 1.040 (t, J = 7.4 Hz, 3 H, C26), 1.003 (s, 3 H, C19), 0.981 (d, J = 6.8 Hz, 3 H, C21), 0.886 (d, J = 6.4 Hz, 3 H, 23-Me), 0.647 (s, 3 H, C18); low-resolution mass spectrum, m/z (relative intensity) 398 (M^+, $C_{28}H_{46}O$, 2), 314 (51), 299 (10), 281 (17), 229 (30), 213 (23), 211 (20), 145 (77), 105 (100), 55 (75).

23-Methyl-27-norergosta-5,24(28)-dien-3β-ol B (60b-N): mp 146–149 °C (MeOH); HPLC t_R 48 min (MeOH), 46 min (MeCN/MeOH/EtOAc); ^{1}H NMR (400 MHz) δ ($CDCl_3$) 5.351 (m, 1 H, C6), 4.717 (s, 1 H, C28), 4.668 (s, 1 H, C28), 1.029 (t, J = 7.4 Hz, 3 H, C26), 1.011 (s, 3 H, C19), 0.968 (d, J = 6.7 Hz, 3 H, C21), 0.917 (d, J = 6.4 Hz, 3 H, 23-Me), 0.701 (s, 3 H, C18); low-resolution mass spectrum, m/z (relative intensity) 398 (M^+, $C_{28}H_{46}O$, 4), 314 (100), 300 (80), 271 (48), 229 (47), 159 (33), 145 (32), 55 (85).

25-(2-Propyl)-27-norcholesta-5,24(*Z*)-dien-3β-ol (62-N): mp 135–136 °C (MeOH); HPLC t_R 56 min (MeOH); ^{1}H NMR (400 MHz) δ ($CDCl_3$) 5.353 (m, 1 H, C6), 5.016 (t, J = 7.0 Hz, 1 H, C24), 1.581 (s, 3 H, C26), 1.007 (s, 3 H, C19), 0.956 (d, J = 6.9 Hz, 6 H), 0.933 (d, J = 6.5 Hz, 3 H), (C21 and CH(CH_3)$_2$), 0.677 (s, 3 H, C18); low-resolution mass spectrum, m/z (relative intensity) 412 (M^+, $C_{29}H_{48}O$, 100), 397 (37), 379 (14), 300 (24), 271 (50), 145 (12), 83 (16), 81 (18), 69 (20), 55 (26).

23-Vinyl-23-methyl-26,27-dinorergost-5-en-3β-ol A (63a-N): mp 180–183 °C (MeOH); HPLC t_R 59.5 min (MeOH); ^{1}H NMR (400 MHz) δ ($CDCl_3$) 5.638 (dd, J = 17.6, 10.8 Hz, 1 H, CHCH$_2$), 5.352 (m, 1 H, C6), 5.020 (d, J = 10.8 Hz, 1 H, CHCH_2), 4.861 (d, J = 17.6 Hz, 1 H, CHCH_2), 0.999 (s, 3 H, C19), 0.940 (d, J = 6.4 Hz, 3 H, C21), 0.884 (s, 3 H, 23-Me), 0.821 (d, J = 6.8 Hz, 3 H, C25 or C28), 0.777 (d, J = 6.8 Hz, 3 H, C25 or C28), 0.656 (s, 3 H, C18); low-resolution mass spectrum, m/z (relative intensity) 412 (M^+, $C_{29}H_{48}O$, 39), 397 (9), 369 (31), 351 (15), 314 (52), 300 (64), 283 (38), 271 (100), 97 (14), 55 (21).

23-Vinyl-23-methyl-26,27-dinorergost-5-en-3β-ol (63b-N): mp 179–181 °C (MeOH); HPLC t_R 61.5 min (MeOH); ^{1}H NMR (400 MHz) δ ($CDCl_3$) 5.762 (dd, J = 17.6, 10.8 Hz, 1 H, CHCH$_2$), 5.351 (m, 1 H, C6), 4.976 (d, J = 10.8 Hz, 1 H, CHCH_2), 4.843 (d, J = 17.6 Hz, 1 H, CHCH_2), 1.001 (s, 3 H, C19), 0.889 (d, J = 6.4 Hz, 3 H, C21), 0.886 (s, 3 H, 23-Me), 0.804 (d, J = 6.8 Hz, 3 H, C25 or C28), 0.782 (d, J = 6.8 Hz, 3 H, C25 or C28), 0.680 (s, 3 H, C18); low-resolution mass spectrum, m/z (relative intensity) 412 (M^+, $C_{29}H_{48}O$, 17), 369 (22), 351 (18), 314 (27), 300 (61), 283 (34), 271 (72), 97 (63), 69 (58), 55 (100).

25-(2-Propyl)-27-norcholesta-5,24(*E*)-dien-3β-ol (64-N): mp 128–129 °C (MeOH); HPLC t_R 56 min (MeOH); ^{1}H NMR (400 MHz) δ ($CDCl_3$) 5.352 (m, 1 H, C6), 5.103 (t, J = 7.0 Hz, 1 H, C24), 1.567 (s, 3 H, C26), 1.008 (s, 3 H, C19), 0.973 (d, J = 6.8 Hz, 6 H), 0.937 (d, J = 6.6 Hz, 3 H) (C21 and CH(CH_3)$_2$), 0.675 (s, 3 H, C18); low-resolution mass spectrum, m/z (relative intensity) 412 (M^+, $C_{29}H_{48}O$, 81), 397 (31), 379 (16), 300 (48), 271 (100), 145 (11), 83 (16), 81 (15), 69 (17), 55 (41).

23,25-Dimethylergosta-5,24(28)-dien-3β-ol A (66a-N): HPLC t_R 55 min (MeOH); ^{1}H NMR (400 MHz) δ ($CDCl_3$) 5.349 (m, 1 H, C6), 4.907 (s, 1 H, C28), 4.732 (s, 1 H, C28).

23,25-Dimethylergosta-5,24(28)-dien-3β-ol B (66b-N): HPLC t_R 55 min (MeOH); ^{1}H NMR (400 MHz) δ ($CDCl_3$) 5.349 (m, 1 H, C6), 4.846 (s, 1 H, C28), 4.689 (s, 1 H, C28).

25-(*tert*-Butyl)-27-norcholesta-5,24(*E*)-dien-3β-ol (67-N): mp 145–146 °C (MeOH); HPLC t_R 55 min (MeOH); ^{1}H NMR (400 MHz) δ ($CDCl_3$) 5.352 (m, 1 H, C6), 5.149 (t, J = 6.4 Hz, 1 H, C24), 1.595 (s, 3 H, C26), 1.013 (s, 9 H, t-Bu), 1.007 (s, 3 H, C19), 0.941 (d, J = 6.4 Hz, 3 H, C21), 0.673 (s, 3 H, C18); low-resolution mass spectrum, m/z (relative intensity) 426 (M^+, $C_{30}H_{50}O$, 100), 411 (12), 393 (12), 314 (24), 300 (26), 281 (14), 271 (24), 95 (24), 81 (22), 57 (23).

23-Vinyl-23,24-dimethyl-26,27-dinorergost-5-en-3β-ol A (68a-N): HPLC t_R 60 min (MeOH); ^{1}H NMR (400 MHz) δ ($CDCl_3$) 5.938 (dd, J = 17.6, 10.9 Hz, 1 H, CHCH$_2$), 5.352 (m, 1 H, C6), 5.005 (d, J = 10.9 Hz, 1 H, CHCH_2), 4.868 (d, J = 17.6 Hz, 1 H, CHCH_2).

23-Vinyl-23,24-dimethyl-26,27-dinorergost-5-en-3β-ol B (68b-N): HPLC t_R 60 min (MeOH); ^{1}H NMR (400 MHz) δ ($CDCl_3$) 5.810 (dd, J = 17.6, 11.0 Hz, 1 H, CHCH$_2$), 5.352 (m, 1 H, C6), 5.065 (d, J = 11.0 Hz, 1 H, CHCH_2), 4.881 (d, J = 17.6 Hz, 1 H, CHCH_2).

25-(1-Methylethenyl)-23-vinylcholest-5-en-3β-ol A (72a-N): HPLC t_R 62 min (MeOH), 74 min (MeCN/MeOH/EtOAc); ^{1}H NMR (400 MHz) δ ($CDCl_3$) 5.654 (ddd, J = 16.8, 10.2, 9.0 Hz, 1 H, vinyl CH), 5.353 (m, 1 H, C6), 4.868 (d, J = 16.8 Hz, 1 H, vinyl CH_2), 4.803 (d, J = 10.2 Hz, 1 H, vinyl CH_2), 1.694 (s, 3 H, terminal methyl), 1.039 (s, 3 H, C26 or C27), 1.021 (s, 3 H, C26 or C27), 1.008 (s, 3 H, C19), 0.904 (d, J = 6.6 Hz, 3 H, C21), 0.685 (s, 3 H, C18); low-resolution mass spectrum, m/z (relative intensity) 452 (M^+, $C_{32}H_{52}O$, 3), 437 (2), 314 (8), 300 (25), 271 (25), 255 (8), 213 (9), 137 (33), 109 (45), 95 (49), 83 (82), 81 (93), 69 (71), 67 (54), 55 (100).

25-(1-Methylethenyl)-23-vinylcholest-5-en-3β-ol B (72b-N): HPLC t_R 62 min (MeOH), 79 min (MeCN/MeOH/EtOAc); ^{1}H NMR (400 MHz) δ ($CDCl_3$) 5.431 (ddd, J = 16.8, 9.7, 9.2 Hz, 1 H, vinyl CH), 5.353 (m, 1 H, C6), 4.873 (d, J = 9.2 Hz, 1 H, vinyl CH_2), 4.850 (d, J = 16.8 Hz, 1 H, vinyl CH_2), 1.687 (s, 3 H, terminal methyl), 1.040 (s, 3 H, C26 or C27), 1.017 (s, 3 H, C26 or C27), 0.999 (s, 3 H, C19), 0.858 (d, J = 6.5 Hz, 3 H, C21), 0.638 (s, 3 H, C18); low-resolution mass spectrum same as for **72a-N**.

26-(1,1,2-Trimethyl-2-propenyl)-27-norcholesta-5,24-dien-3β-ol (73-N): mp 87–90 °C (MeOH); HPLC t_R 72.5 min (MeOH); ^{1}H NMR (400 MHz) δ ($CDCl_3$) 5.351 (m, 1 H, C6), 5.346 (dt, J = 15.0, 7.0 Hz, 1 H, C24 or C25), 5.252 (dt, J = 15.0, 7.0 Hz, 1 H, C24 or C25), 4.718 (s, 1 H, propenyl CH_2), 4.669 (s, 1 H, propenyl CH_2), 2.021 (d, J = 6.7 Hz, 2 H, C26), 1.719 (s, 3 H, terminal methyl), 1.002 (s, 9 H, C19 and geminal methyls), 0.902

(d, J = 6.5 Hz, 3 H, C21), 0.669 (s, 3 H, C18); low-resolution mass spectrum, m/z (relative intensity) 452 (M^+, $C_{32}H_{52}O$, 2), 437 (2), 314 (8), 299 (5), 271 (16), 255 (5), 83 (100), 69 (10), 55 (22).

Dimer (74-M): R_f = 0.59 (hexanes/ether, 9:1); ^1H NMR (400 MHz) δ ($CDCl_3$) 3.323 (s, 6 H, OMe), 1.019 (s, 6 H, C19), 0.884 (d, J = 6.4, 6 H, C21), 0.712 (s, 6 H, C18); low-resolution mass spectrum, m/z (relative intensity) 658 (M^+, $C_{46}H_{74}O_2$, 6), 643 (7), 603 (20), 255 (10), 145 (17), 95 (30), 71 (98), 55 (99), 42 (100).

THF adduct A (75a-M): R_f = 0.33 (hexanes/ether, 9:1); ^1H NMR (400 MHz) δ ($CDCl_3$) 3.862 (m, 2 H, THF C4), 3.691 (q, J = 7.4 Hz, 1 H, THF C2), 3.323 (s, 3 H, OMe), 1.017 (s, 3 H, C19), 0.974 (d, J = 5.9 Hz, 3 H, C21), 0.721 (s, 3 H, C18); low-resolution mass spectrum, m/z (relative intensity) 400 (M^+, $C_{27}H_{44}O_2$, 8), 385 (7), 368 (10), 345 (12), 111 (35), 105 (24), 91 (22), 71 (100), 55 (23).

THF adduct B (75b-M): R_f = 0.26 (hexanes/ether, 9:1); ^1H NMR (400 MHz) δ ($CDCl_3$) 3.866 (m, 2 H, THF C4), 3.690 (q, J = 7.4 Hz, 1 H, THF C2), 3.315 (s, 3 H, OMe), 1.012 (s, 3 H, C19), 0.969 (d, J = 6.6 Hz, 3 H, C21), 0.740 (s, 3 H, C18); low-resolution mass spectrum, m/z (relative intensity) 400 (M^+, $C_{27}H_{44}O_2$, 7), 385 (6), 368 (6), 345 (10), 111 (29), 105 (23), 91 (22), 71 (100), 55 (23).

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Electronic and Steric Control of α- versus β-Naphthyl Migratory Aptitudes in Enone Photochemistry. Mechanistic and Exploratory Organic Photochemistry[1,2]

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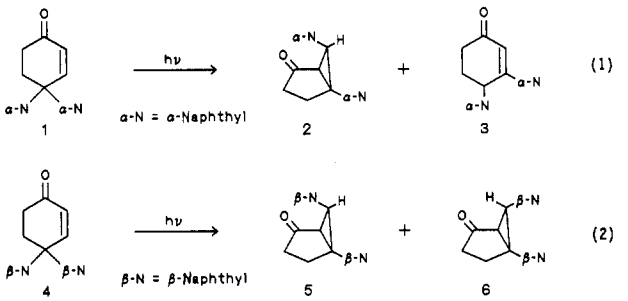
The photochemistry of 4-α-naphthyl-4-β-naphthylcyclohexenone was investigated. Photolysis afforded endo and exo isomers of 5-α-naphthyl-6-β-naphthylbicyclo[3.1.0]-2-hexanone and 5-β-naphthyl-6-α-naphthylbicyclo[3.1.0]-2-hexanone as well as 3-β-naphthyl-4-α-naphthyl-2-cyclohexenone. The reaction was highly stereoselective with the 6-*endo*-naphthyl product being preferred both in the 6-α-naphthyl and the 6-β-naphthyl cases. Quantum yields were determined for the direct and sensitized reactions. In direct irradiations a ratio of 48:52 was observed for α- to β-naphthyl migration products while in sensitized photolyses the ratio was 41:59. Despite the differences between direct and sensitized runs, quenching studies revealed that the reacting species were triplets throughout. Excited-state triplet decay and reaction rates were determined. Interestingly, evidence was adduced for differential local excitation of α- and β-naphthyl moieties depending on the mode of energy transfer. A stereoselective triplet transfer from enone triplet to axial naphthyl in the direct irradiations and a statistical triplet excitation of axial and equatorial naphthyl groups in sensitization accounts for the results. Conformational information bearing on the photochemistry was obtained from molecular mechanics calculations.

Introduction

Since our discovery two and a half decades ago of the rearrangement of 4-arylcyclohexenones,[3] we have endeavored to expand the scope of the reaction and our understanding of its mechanistic details. Most recently, we reported[3g] the rearrangements of the 4,4-di-α-naphthyl- and 4,4-di-β-naphthylcyclohexenones (**1** and **4**, respectively) as in eq 1 and 2. The rearrangement of the α-naphthyl enone **1** was observed to proceed with ca. twice the efficiency and three times the triplet rate of the β-naphthyl enone **4**.



It was of considerable interest to compare α-naphthyl and β-naphthyl migratory aptitudes intramolecularly. Hence we proceeded to investigate the photochemistry of 4-α-naphthyl-4-β-naphthyl-2-cyclohexenone (**7**).

Results

Synthesis of Photochemical Reactant and Two Potential Photoproducts. The synthesis of the dinaphthyl enone **7** is outlined in Scheme I. Also included in the scheme is the preparation of two potential photoproducts, 3-α-naphthyl-4-β-naphthyl-2-cyclohexenone (**14**) and 3-β-naphthyl-4-α-naphthyl-2-cyclohexenone (**15**). A few points require comment. First, although the cis oxirane **8** is depicted, the corresponding trans isomer rearranged with equal facility and yield to afford aldehyde **9**. Also, the synthesis of the 3,4-enones **14** and **15** differed

(1) This is Paper 156 of our photochemical series and Paper 215 of the general series.

(2) (a) For Paper 213, see: Zimmerman, H. E.; Weber, A. M. *J. Am. Chem. Soc.* **1988**, *110*, 995-1007. (b) For Paper 214, see: Zimmerman, H. E.; Oaks, F. L.; Campos, P. *J. Am. Chem. Soc.* **1988**, *110*, 1007-1018.

(3) (a) Zimmerman, H. E.; Wilson, J. W. *J. Am. Chem. Soc.* **1964**, *86*, 4036-4042. (b) Zimmerman, H. E.; Hancock, K. G. *J. Am. Chem. Soc.* **1968**, *90*, 3749-3760. (c) Zimmerman, H. E.; Rieke, R. D.; Scheffer, J. R. *J. Am. Chem. Soc.* **1967**, *89*, 2033-2047. (d) Zimmerman, H. E.; Lewin, N. *J. Am. Chem. Soc.* **1969**, *91*, 879-886. (e) Zimmerman, H. E.; Elser, W. R. *J. Am. Chem. Soc.* **1969**, *91*, 887-896. (f) Zimmerman, H. E.; King, R. K.; Xu, J.-H.; Caufield, C. E. *J. Am. Chem. Soc.* **1985**, *107*, 7724-7732. (g) Zimmerman, H. E.; Caufield, C. E.; King, R. K. *J. Am. Chem. Soc.* **1985**, *107*, 7732-7744. (h) Also, note that 4-arylcyclopentenones undergo a related rearrangement.[4]

(4) (a) Zimmerman, H. E.; Little, R. D. *J. Chem. Soc., Chem. Commun.* **1972**, 698-700. (b) Zimmerman, H. E.; Little, R. D. *J. Am. Chem. Soc.* **1974**, *96*, 4623-4630. (c) Wolff, S.; Agosta, W. C. *J. Chem. Soc., Chem. Commun.* **1972**, 226-227.

0022-3263/89/1954-2125$01.50/0