ical Works) that had been dried by azeotropic distillation. Matched silica cells (5 cm) were employed and the spectra were recorded on a Beckman Model IR-12 spectrometer in the region 3100–3700 cm^{-1}. The single beam–double beam ratio was adjusted to 1 at a base line of 90% transmittance. The base line was determined with both cells containing the solvent at a scanning speed of 70 cm^{-1}/min. Several milliliters of solvent were then removed by syringe from the sample cell, the alcohol was quickly transferred to the cell, and the solvent was replaced. The cell was stoppered and gently shaken to achieve a homogeneous solution. The spectrum was then recorded at a scanning speed of 70 cm^{-1}/min. All samples were run at room temperature, *i.e.*, 23°. Using identical instrument parameters good reproducibility of spectra was observed.

In the *threo* amino alcohols **1a–d** the peak position of the broad OH···N band could be estimated to an accuracy of about ±2.5 cm^{-1} directly from the spectra. Peak positions of the multicomponent curves (Figure 2) of the *erythro* amino alcohols **1a–d** and 1,2-diphenylethanol (**3**) were assigned after resolution by a special-purpose analog computer, the Du Pont 310 curve resolver. In generating each component of the curve, shapes corresponding to Gaussian distribution were assumed. The positions of the resolved, relatively sharp unassociated OH and OH···π peaks could be estimated to ±1.5 cm^{-1}; the broad OH···N peak was estimated to an accuracy of ±2.5 cm^{-1}. Extinction coefficients were measured by employing peak height. The resolved curve was used to measure peak heights in the case of multicomponent absorption curves.

Registry No.—**1a** (*threo*), 19640-34-7; **1a** (*erythro*), 19640-35-8; **1b** (*threo*), 19640-36-9; **1b** (*erythro*), 19640-37-0; **1c** (*threo*), 19640-38-1; **1c** (*erythro*), 19640-39-2; **1d** (*threo*), 2576-07-0; **1d** (*erythro*), 19640-41-6; **2** (*trans*), 7581-94-4; **3**, 614-29-9; **4**, 98-85-1.

Acknowledgment.—The support of one of the authors (M. K. M.) through an NDEA predoctoral fellowship (1963–1966) is gratefully acknowledged. The authors wish to thank Dr. H. J. Sloane for his helpful suggestions in running the high-dilution infrared spectra.

Alumina-Catalyzed Dehydration of Methylhexadienols. A Reinvestigation[1]

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Catalytic dehydration of substituted hexadienols usually produces a mixture of substituted 1,3,5-hexatrienes and the corresponding substituted 1,3-cyclohexadienes. Alumina dehydration of 1,5-heptadien-4-ol or 3-methyl-1,5-hexadien-3-ol at temperatures ranging from 250 to 350° yielded the expected methyltrienes, but the cyclohexadiene fraction consisted of double-bond isomers whose distribution proved to be temperature dependent. Thermolysis of authentic 1,3,5-heptatriene or 3-methyl-1,3,5-hexatriene over alumina or glass helices yielded similar results. The 1,3-cyclohexadienes formed at 250° can be predicted on the basis of electrocyclic ring closure of an intermediate triene having a *cis* configuration about the central double bond. At 350°, 1,3-cyclohexadiene mixtures, resulting from intramolecular 1,5-hydrogen shifts in the Woodward–Hoffmann product, predominate.

Until very recently, the preparation of substituted 1,3,5-hexatrienes has involved either a vapor phase catalytic dehydration over alumina or an acid-catalyzed dehydration of an appropriately substituted hexadienol. The products isolated from these procedures, in most cases, have been of doubtful purity. Pure substituted 1,3,5-hexatrienes have been prepared by means of a Hofmann elimination.[2–4] It has been established that the major by-product of catalyzed hexadienol dehydration is a corresponding cyclohexadiene. The formation of these cyclohexadienes has been described by Woods and coworkers,[5,6] who considered thermal trienic ring closure an internal Diels–Alder reaction. However, Woodward and Hoffmann[7] now describe it as a disrotatory electrocyclic transformation.

Woods and Fleishacker[5] attempted the preparation of the three possible methyl-1,3,5-hexatrienes by dehydration of appropriately substituted hexadienols over alumina, however, only 1,3,5-heptatriene was obtained in a relatively pure state. The 2-methyl- and 3-methyl-1,3,5-hexatrienes were apparently contaminated with appreciable quantities of methylcyclohexadienes. These workers also reported that either dehydration of the methylhexadienol over alumina at 500° or passage of methyl-1,3,5-hexatriene over the catalyst under the same conditions yielded methylcyclohexadienes of indeterminate double-bond position. We have recently shown[8] that under the experimental conditions employed by Woods and Fleischacker, cyclization followed by dehydrogenation to toluene is also an important reaction. Hence, it is probable that products formed at these temperatures were contaminated with toluene.

Lewis and Steiner[9] have studied the cyclization of 1,3,5-hexatriene and found that the purely thermal cyclization of the *cis* isomer was practically quantitative at 120–190°; the *trans* isomer was unaffected. We decided, therefore, to reinvestigate both the catalytic dehydration of methylhexadienols and the thermal cyclization of the pure methyl-1,3,5-hexatrienes at temperatures lower than those employed by Woods, *et al.*, in order to suppress the methylcyclohexadiene to toluene reaction. We also hoped to elucidate the structures of the methyl cyclohexadienes formed in both of the above reactions.

Both 1,5-heptadien-4-ol (**1**) and 3-methyl-1,5-hexadien-3-ol (**2**) were dehydrated in the vapor phase over activated alumina at 250° and at 350°. Table I summarizes the products obtained from these dehydrations.

Application of earlier[5–9] observations on dienol dehydration to the alumina-catalyzed dehydration of either **1** or **2** would lead one to predict the reaction sequences given in Scheme I. Although most previous

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(1) (a) Portions of this paper were presented at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968. (b) The authors would like to express their appreciation to the National Science Foundation for partial support of this research under an Undergraduate Research Participation Grant.

(2) C. W. Spangler and G. F. Woods, *J. Org. Chem.*, **28**, 2245 (1963).

(3) C. W. Spangler and G. F. Woods, *ibid.*, **30**, 2218 (1965).

(4) J. C. H. Hwa, P. L. de Benneville, and H. J. Sims, *J. Amer. Chem. Soc.*, **82**, 2537 (1960).

(5) H. Fleischacker and G. F. Woods, *ibid.*, **78**, 3436 (1956).

(6) G. F. Woods and A. Viola, *ibid.*, **78**, 4380 (1956).

(7) R. B. Woodward and R. Hoffmann, *ibid.*, **87**, 395 (1965).

(8) C. W. Spangler, *J. Org. Chem.*, **31**, 346 (1966).

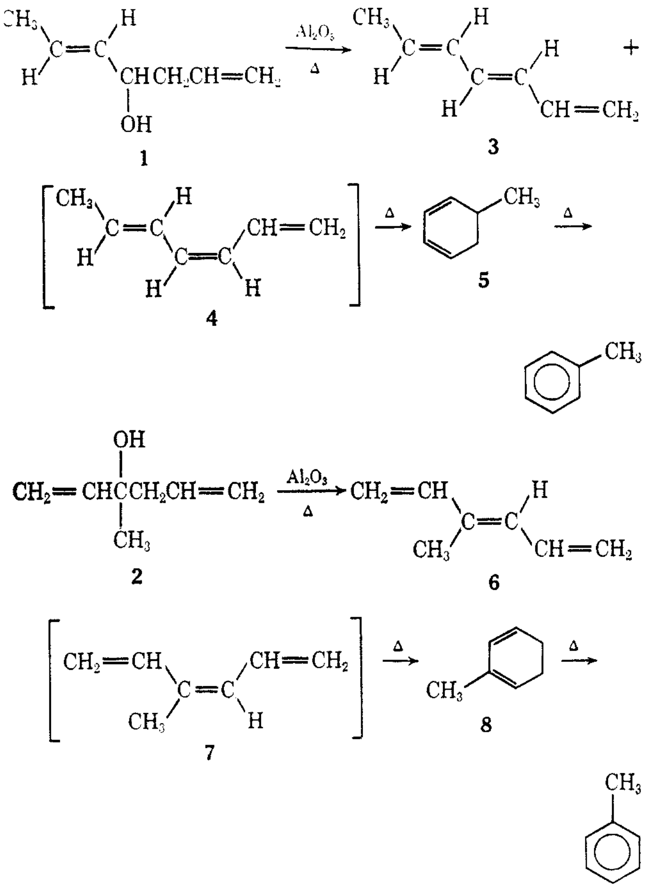
(9) K. E. Lewis and H. Steiner, *J. Chem. Soc.*, 3080 (1964).

TABLE I
METHYLHEXADIENOL–ALUMINA DEHYDRATION PRODUCTS

		% of total product[a]					
		1,3,5-Triene		1,3-Cyclohexadiene			
Dienol	Temp, °C	1-Me	3-Me	1-Me	2-Me	5-Me	Toluene
1	250	62[b]		Trace	Trace	35	Trace
1	350	31[c]		18	11	29	Trace
2	250		26[d]	3	25	31	3
2	350		22[e]	24	20	11	4

[a] Several minor products (*ca.* 1–2% each) make up the balance of products. 3-Methylenecyclohexene was present in each dehydration product (1–4%). [b] 78% *trans, trans*, 22% *cis, trans.* [c] 68% *trans, trans*, 32% *cis, trans.* [d] *cis–trans* peaks not totally resolved. [e] *trans* isomer at least 90% of mixture.

SCHEME I

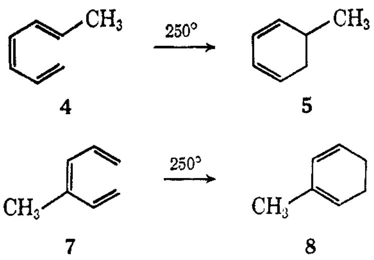


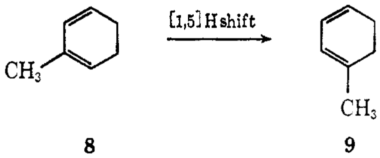
workers have failed to detect the labile trienes having a *cis* configuration about the central double bond, they have found considerable quantities of the corresponding 1,3-cyclohexadienes. If the above reaction scheme is correct, then the quantity of cyclized product found in dienol dehydrations may be utilized to indicate the ratio of *cis* to *trans* product in the original dehydration step. However, there have been no definitive experiments to determine if *cis–trans* triene mixtures actually follow the on-column cyclization sequence postulated in dienol dehydration.

Thermolyses of pure 1,3,5-heptatriene[3] (56% **3**, 44% **4**) or of 3-methyl-1,3,5-hexatriene[3] (55% **6**, 45% **7**) in a dehydration column packed with either glass helices or with activated alumina were carried out under reaction conditions essentially identical with those employed for the dehydration of either **1** or **2**. Table II summarizes the results of these comparative cyclizations.

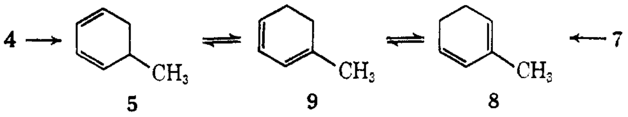
It can immediately be seen that thermolyses carried out at 250° tend to support the proposed dehydration scheme. The methyl-1,3-cyclohexadiene obtained from both **4** and **7** has the double bond positional structure expected from simple electrocyclic ring closure (**5** and **8**, respectively) (Scheme II). However, other processes apparently can occur simultaneously when alumina replaces Pyrex as a thermolysis solid support. Thus 1-methyl-1,3-cyclohexadiene (**9**) and 3-methylenecyclohexene (**10**) appear in the 250° alumina thermolysis product of 3-methyl-1,3,5-hexatriene. The formation of **10** has been noted previously in similar systems by Pines, *et al.*,[10,11] and should not be surprising. However, **9** cannot result from a simple ring-closing process of **7**. The most probable source of this abnormal cyclization product is **8**, from which **9** can result by a [1,5] sigmatropic shift of hydrogen. Another alumina process which must exist in order to account for the sum total of cyclization products is *trans* → *cis* isomer interconversion. That this is not a thermal process at 250° is evident from a material balance; the quantity of cyclization product formed is directly related to the initial central double bond *cis*-isomeric content. This conversion is appreciable at 250° over alumina: **3** → **4** → products (28.6%),[12] and **6** → **7** → products (32.8%).[12]

SCHEME II





At 350°, thermolysis over Pyrex helices more closely resembles the alumina process than at 250°. In both cases, the cyclization products are complex mixtures of the three possible methyl-1,3-cyclohexadienes and/or 3-methylenecyclohexene and toluene. The residual yields of the corresponding 1,3,5-trienes are also considerably reduced. Thus cyclization followed by [1,5] hydrogen shifts predominates. Similarly, at 350°, *trans* → *cis* conversion followed by cyclization becomes important in the purely thermal reaction over helices. Toluene formation is also evident at 350°, although it is a minor process compared to its importance at higher temperatures.[8]



Catalytic dienol dehydration processes, and the resultant complex product mixtures, thus can be readily interpreted on the basis of the above studies. Dehydra-

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(10) H. Pines and R. H. Kozlowski, *J. Amer. Chem. Soc.*, **78**, 3776 (1955).

(11) H. Pines and C. Chen, *ibid.*, **81**, 928 (1958).

(12) Percentages indicate quantity of original central *trans* isomer following this process *via a vis* 0% for the purely thermal process over helices.

TABLE II
THERMOLYSIS METHYL-1,3,5-HEXATRIENES

1,3,5-Triene	Temp, °C	Support	% of total[c] 3	4	6	7	5	8	9[a]	10[b]
1-Me (56% **3**, 44% **4**)	250	Helices	56	22			22			
	250	Al_2O_3	40	18			42		Trace	
	350	Helices	45	10			15	8	22	
	350	Al_2O_3[d]	8	4			21	25	29	8
3-Me (55% **6**, 45% **7**)	250	Helices			55	Tr	Tr	45	Tr	
	250	Al_2O_3			37	Tr	Tr	40	13	10
	350	Helices			43	Tr	1	44	12	
	350	Al_2O_3[e]			20	Tr	6	26	32	9

[a] **9**, 1-methyl-1,3-cyclohexadiene. [b] **10**, 3-methylenecyclohexene. [c] Several minor products (*ca.* 1–2% each) were present in those thermolysis products totalling less than 100%. [d] Toluene, 5% of product. [e] Toluene, 7% of product.

tions in which the central trienic double bond is generated yield an initial mixture of geometric isomers. This mixture can contain appreciable quantities of the less stable *cis* isomers. At the reaction temperatures of most catalytic dehydrations, however, electrocyclic ring closure of the *cis* isomer is a highly favored reaction, and usually little, if any, *cis* isomer survives.[13] Unfortunately, the total quantity of cyclized product is not a reliable measure of the initial *cis*/*trans* product ratio, since alumina can catalyze *trans* → *cis* conversion, even at 250°. In most cases the predominating, if not sole, cyclization product at 250° will be a 1,3-cyclohexadiene arising from electrocyclic ring closure of the *cis*-triene. However, at elevated temperatures (350° or higher), other processes predominate: (1) substituted 1,3-cyclohexadienes undergo thermal [1,5] sigmatropic rearrangement resulting in a mixture of positional isomers[14]; (2) extensive *trans* → *cis* → cyclization takes place, thus reducing the yield of triene considerably; (3) dehydrogenation of intermediate cyclohexadienes yields aromatics, apparently catalyzed by alumina rather than by thermal means. Although the mechanism by which some of these products, and the nature of some minor processes, are still obscure, we feel that these studies extend our understanding of the catalytic dehydration of unsaturated alcohols considerably.

Experimental Section[15]

Dehydration of 1,5-Heptadien-4-ol (1). **A.**—Through a 22-mm Pyrex tube packed to a depth of 12 in. with activated alumina (8–14 mesh), and externally heated at 250° with a Lindberg Hevi-Duty split-tube electric furnace, was dropped 1,5-heptadien-4-ol (21.3 g, 0.19 mol) at the rate of 0.5 ml/min. The alumina had been dried previously by heating the column at 300° under vacuum for 1 hr. A pressure of 20–25 mm was maintained in the system to facilitate rapid removal of the product from the column.[16] The product was trapped in a flask immersed in a Dry Ice–acetone bath, and subsequently warmed to room temperature and separated from a small quantity of water by filtration through anhydrous magnesium sulfate. After filtration, the clear yellow liquid was distilled at reduced pressure and the volatile fraction collected. No attempt was made to maximize the yield (75%) and a substantial quantity of liquid was allowed to remain in the distillation flask due to the possibility of cyclohexadiene peroxide formation reported by Woods and Fleischacker.[5] Glpc analysis showed the presence of three products. The peak emanating from the chromatograph representing the supposed methylcyclohexadiene was trapped in a V tube immersed in a Dry Ice bath. Reinjection of this sample under conditions known to allow the separation of all isomeric methylcyclohexadienes showed that it was free of triene and was 98+% pure. For this product, $n^{25}{}_D$ 1.4628, λ_{max} 259 mμ (ϵ_{max} 3700) was compared to that reported by Woods, *et al.*[5] [$n^{28}{}_D$ 1.474 and λ_{max} 259 (ϵ_{max} 3300)]. The nmr spectrum revealed a doublet at τ 8.8 (three methyl protons, J = 5.5 Hz), multiplet 7.3–8.0 (three allylic protons), multiplet 3.8–4.3 (four vinyl protons). This compares favorably with 1,3-cyclohexadiene, τ 7.8–7.9 (four allylic protons) and 3.9–4.2 (four vinyl protons). The infrared spectrum was consistent with the assigned structure. On the basis of the above we assign the structure as 5-methyl-1,3-cyclohexadiene (**5**).

B.—1,5-Heptadien-4-ol (20.0 g, 0.18 mol) was dehydrated, as described above, at 350°. The crude product was isolated and purified (85% yield). Glpc analysis revealed that at least 13 components were present in the product mixture. Six of these minor constituents (6.4% of total) were not identified. The C_7H_{10} isomers were separated from the gc effluent as described above and analyzed by uv, ir, and nmr spectrometry. In general, a rapid qualitative analysis could be made based on uv maxima (λ_{max} mμ (isooctane) is given in parentheses): **5** (259), **8** (261), **9** (264), **10** (232). The ir and nmr spectra of all C_7H_{10} isomers were consistent with this assignment.

Dehydration of 3-Methyl-1,5-hexadien-3-ol (2). **A.**—3-Methyl-1,5-hexadien-3-ol (**2**, 8.0 g, 0.071 mol) was dehydrated, as described above, at 250° yielding a crude product mixture (4.8 g, 72%) which upon glpc analysis was shown to consist of at least 12 components. Five of these minor constituents (8–9% of total) were not identified.

B.—3-Methyl-1,5-hexadien-3-ol (**2**, 5.0 g, 0.045 mol) was dehydrated, as described above, at 350° yielding a crude product mixture (3.0 g, 71%) which upon glpc analysis was shown to consist of at least 12 components. Five of these minor constituents (15% of total) were not identified.

Cyclization of 1,3,5-Heptatriene (3, 4). **A.**—A mixture of 56% *trans,trans* **3** and 44% *cis,trans*-1,3,5-heptatriene (**4**, 9.0 g) was added dropwise through a 22-mm Pyrex tube packed to a depth of 12 in. with $^1/_{16}$ in. Pyrex helices and externally heated at 250° as in the above dehydration studies. The thermolysis product was isolated in a manner similar to the above dehydrations, finally yielding a product composed of 56% *trans,trans*-, 22% *cis,trans*-1,3,5-heptatriene and 22% 5-methyl-1,3-cyclohexadiene (**5**), as determined by glpc (63% recovery).

B.—A similar thermolysis at 350° yielded 45% *trans,trans*-, 10% *cis,trans*-1,3,5-heptatriene 15% **5**, 8% **8**, and 22% **10** (72% recovery).

C.—A similar thermolysis at 250°, except that activated alumina (8–14 mesh) was utilized instead of Pyrex helices, yielded 40% *trans,trans*- 18% *cis,trans*-1,3,5-heptatriene and 42% **5** (65% recovery).

D.—A thermolysis similar to **C** at 350° yielded 8% *trans,-trans*-, 4% *cis,trans*-1,3,5-heptatriene, 21% **5**, 25% **8**, and 29% **9** as well as several minor products (60% recovery).

Cyclization of 3-Methyl-1,3,5-hexatriene (6, 7). **A.**—A mixture of 55% *trans*- and 45% *cis*-3-methyl-1,3,5-hexatriene (10.0 g) was added to the above described thermolysis column

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[13] A suggestion by a referee which we reject is that the *cis–trans* ratio triene observed at any dehydration temperature, *T*, might well represent the equilibrium ratio, *K*. As can be seen from our data, however, the experimental ratio varies considerably from dehydration to thermolysis.

[14] For an excellent review of thermal [1,5] hydrogen shifts, see the following, and references therein: (a) D. S. Glass, R. S. Boikess, and S. Winstein, *Tetrahedron Lett.*, 999 (1966); (b) K. W. Egger, *J. Amer. Chem. Soc.*, **89**, 3688 (1967).

[15] Gas–liquid partition chromatography was performed with an Aerograph Model 202-1B with dual 15-ft, 15% β,β'-oxydipropionitrile-on-Chromosorb W columns. This instrument was equipped with a Disc integrator for peak area measurement. Ultraviolet spectra were obtained with a Perkin-Elmer Model 202 spectrophotometer (Spectrograde isooctane), infrared spectra with a Beckman IR-8. Nmr spectra were obtained with a Varian A-60A spectrometer using TMS (τ 10) as an internal standard and $CDCl_3$ solvent. Activated alumina utilized in these experiments was Matheson Coleman and Bell grade (8–14 mesh) and was not treated further.

[16] Contact time of the alcohol vapor with the alumina catalyst averages between 45 and 60 sec.

packed with helices and maintained at 250°. The products were isolated in a similar manner, yielding 55% *trans*-3-methyl-1,3,5-hexatriene and 45% 2-methyl-1,3-cyclohexadiene (**8**, 74% recovery).

B.—A similar thermolysis at 350° yielded 43% *trans*-3-methyl-1,3,5-hexatriene, 1% **5**, 44% **8**, and 12% **9** (78% recovery).

C.—A similar thermolysis at 250°, except that activated alumina (8–14 mesh) was utilized instead of Pyrex helices, yielded 37% *trans*-3-methyl-1,3,5-hexatriene, 40% **8**, and 13% **9** as well as several minor products (65% recovery).

D.—A thermolysis similar to **C** at 350° yielded 20% *trans*-3-methyl-1,3,5-hexatriene, 6% **5**, 26% **8**, and 32% **9** as well as several minor products (72% recovery).

Registry No.—**5**, 19656-98-5; **8**, 1489-57-2; **9**, 1489-56-1; **10**, 1888-90-0.

The Chemistry of 10α-Estr-4-en-17β-ol-3-one and Selected Transformation Products[1]

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Hydrogenation of estra-4,9(11)-dien-17β-ol-3-one (**1**) gave 10α-estr-4-en-17β-ol-3-one (**2**), the parent member of a new series of steroids. Spectral studies indicate that ring B in this series has a boat conformation. This strained system is readily isomerized to 19-nortestosterone in acids and in base. Reduction with lithium aluminum tri-*t*-butoxyhydride gave the corresponding equatorial 3α-alcohol **7**, which was converted into the 3-deoxy-Δ^4 and -$\Delta^{5(6)}$ olefinic analogs by hydrogenolysis with lithium in ethylamine. The C-4 double bond appears to shift to the corresponding C-5(6) olefin in the presence of strong base. Reduction of **2** with lithium–ammonia solutions gave 10α,5β-estra-17β-ol-3-one (**10**).

Alteration of one or more of the asymmetric centers in the steroid nucleus has led to some interesting changes in its chemical and biological properties.[2] In the present study we would like to describe the synthesis and chemistry of 10α-estr-4-en-17β-ol-3-one (**2**) and of some of its derivatives.

The introduction of the 10α stereochemistry in the estrene nucleus was readily accomplished by selective catalytic hydrogenation of the 9(10) double bond of estra-4,9(10)-dien-17β-ol-3-one (**1**),[3] using as catalyst either palladium on barium sulfate or 2% palladium on strontium carbonate in benzene.[4] The latter resulted in a high degree of selectivity, giving directly in 60% yield a dihydro product which was identified as 10α-estr-4-en-17β-ol-3-one (**2**). In general, all other catalysts and reaction conditions studied gave significant quantities of mixed tetrahydro and aromatized steroids.

Spectral properties of **2** displayed features characteristic of a 19-nortestosterone derivative.[5] Inspection of ORD and CD spectra using dioxane as solvent showed a small negative Cotton effect in the $\pi-\pi^*$ region, a result similar to that reported for 10α-testosterone.[6,7] Surprisingly, a small positive Cotton effect was obtained in this region with methanol.[8] The sign of the Cotton effect in the $n-\pi^*$ region is negative in both solvents. This change in sign in the low-wavelength region can be attributed to a solvation effect. Alternately, and perhaps more likely, a shift in the conformer populations may occur upon changing polarity. Neither 19-nortestosterone nor its 9β,10α-isomer exhibit this behavior. Examination of Dreiding models of **2** revealed that the A ring is relatively flat and can readily assume a positive or a negative chirality. The RD results obtained in dioxane, when analyzed using the chirality rule,[7] are best accommodated by assignment of 10α stereochemistry to the dihydro product **2**. The most plausible conformation consistent with these data is shown in Figure 1. The nmr spectrum of **2** reflects a greater degree of shielding of the C-18 methyl groups by its greater proximity to the C–C bonds in rings A and B resulting in a net diamagnetic shielding, relative to its 10β isomer **5**.[9] The chemical shifts of the C-18 methyl groups of several of the 10α-estrenes reported in this study are shown in Table I, together with those of some corresponding 10β analogs.

The steric strain resulting from the ring-B boat conformation can be readily relieved by enolization and reprotonation at C-10β to give 19-nortestosterone (**5**) after acid or base treatment.[10,11] The configuration of the C-9 proton was therefore confirmed by the isolation of **5** and confirmed further by the hydrogenation of **2** to give the known 10α ketone **6**.[2g,h]

The monoacetate **3**, which could also be obtained by hydrogenation of the diene acetate **4**, was reduced with

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[1] For a preliminary report regarding part of the present work see E. Farkas, J. M. Owen, M. Debono, R. M. Molloy, and M. M. Marsh, *Tetrahedron Letters*, 1023 (1966).

[2] For some recent examples of syntheses of steroids bearing unnatural stereochemistry at one or more asymmetric centers, see (a) P. Westerhof and E. H. Reerink, *Rec. Trav. Chim. Pays-Bas*, **79**, 771 (1960); (b) R. Wenger, H. Dutler, H. Wehrli, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **45**, 2420 (1962), and **46**, 1096 (1963); (c) L. Velluz, G. Nominé; R. Bucourt, A. Pierdet, and J. Tessier, *Compt. Rend.*, **252**, 3903 (1961); (d) J. A. Edwards, P. Crabbé, and A. Bowers, *J. Amer. Chem. Soc.*, **85**, 3313 (1963); (e) P. Westerhof, *Rec. Trav. Chim. Pays-Bas*, **83**, 1069 (1964); (f) F. Sondheimer, R. Mechoulam, and M. Sprecher, *Tetrahedron*, **20**, 2473 (1964); (g) R. T. Rapala and E. Farkas, *J. Org. Chem.*, **23**, 1404 (1958); (h) R. E. Counsell, *Tetrahedron*, **15**, 202 (1961).

[3] M. Perelman, E. Farkas, E. J. Fornefeld, R. J. Kraay, and R. T. Rapala, *J. Amer. Chem. Soc.*, **82**, 2402 (1960).

[4] R. B. Woodward, F. Sondheimer, D. Taub, K. Heusler, and W. M. McLamore, *ibid.*, **74**, 4223 (1952).

[5] (a) A. J. Birch, *J. Chem. Soc.*, 367 (1950); (b) A. L. Wilds and N. A. Nelson, *J. Amer. Chem. Soc.*, **75**, 5366 (1953).

[6] See ref 2b.

[7] W. Moffit, R. B. Woodward, A. Moscowitz, W. Klyne, and C. Djerassi, *J. Amer. Chem. Soc.*, **83**, 4013 (1961).

[8] A. Moscowitz, K. M. Wellman, and C. Djerassi, *Proc. Natl. Acad. Sci. U. S.*, **50**, 799 (1963).

[9] Shielding of hydrogen nuclei in rigid systems is believed to be due to diamagnetic anisotropic contributions associated with neighboring C–C bonds; see L. M. Jackman and R. H. Wiley, *J. Chem. Soc.*, 2881 (1960). For other leading references see J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. II, Permagon Press, New York, N. Y., 1966.

[10] This transformation has precedence in the base-catalyzed epimerization of the C-6 methyl group in the 6β-methyl-Δ^4-3-one system; see ref 11.

[11] A. Bowers and H. J. Ringold, *J. Amer. Chem. Soc.*, **80**, 3091 (1958); H. J. Ringold, E. Batres, and G. Rosenkranz, *J. Org. Chem.*, **22**, 99 (1957).