

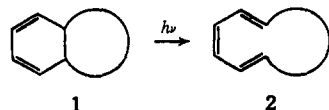
Photochemistry of 9,10-Dimethyl- $\Delta^{1,3}$ -hexalins and Related Steroids. The Role of Ground-State Conformations in Accordant Processes¹

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Abstract: Irradiation of *trans*-9,10-dimethyl- $\Delta^{1,3}$ -hexalin and of the related 5 α -methyl- $\Delta^{1,3}$ -androstadien-17 β -ol acetate rapidly established a photoequilibrium between the diene and the related *trans,cis,trans*-cyclodeca-1,3,5-triene valence isomer. Irradiation of *cis*-9,10-dimethyl- $\Delta^{1,3}$ -hexalin and the related 5 β -methyl- $\Delta^{1,3}$ -androstadien-17 β -ol acetate yielded minor amounts of the *trans,cis,cis* triene. The major products were materials possessing a bicyclo[3.1.0]hex-2-ene nucleus, expected photoproducts of the triene, and the isomerized *trans,cis,trans* triene and its related photoproducts. These results have been explained on the basis of a ground state conformation control of the accordant ring opening process. Of particular interest were the findings of the high degree of thermal stability of the trienes. The stability was related to the steric hindrance to ring closure *via* a disrotatory process. The role of the substituents in these ground-state processes was discussed.

The photoinduced valence isomerization of a 1,3-cyclohexadiene chromophore to a 1,3,5-hexatriene system has been extensively studied from the viewpoint of the relationship of this reaction sequence to the formation of vitamin D.³ More recently, this photochemical sequence has been utilized for the preparation of medium-ring compounds **2** from their



related substituted bicyclo[4.*n*.0]-2,4-diene **1**, typical examples being the synthesis of a 1,3,5-cyclodecatriene related to the sesquiterpene dihydrocostunolide⁴ and the synthesis of 1,3,5-cyclononatriene.^{5,6} In related reversible photochemical isomerization processes, it has been shown that the substitution pattern of the chromophoric system plays an important role in the photoequilibrium reached by affecting the conformation of the triene formed.⁷ Since both photochemical and thermal valence isomerizations follow the general orbital symmetry concepts,⁸ it would be anticipated that in medium-ring systems the substitution effect would be especially important. To evaluate such effects, the 9,10-dimethyl- $\Delta^{1,3}$ -hexalin system⁹ and the related steroid series have been studied.

(1) This work was supported in part by the National Institute of Arthritis and Metabolic Diseases, U. S. Public Health Service, Grant No. AM-00709; and the Hoffmann-La Roche Foundation.

(2) (a) National Science Foundation Predoctoral Fellow; (b) National Institutes of Health Postdoctoral Fellow.

(3) For a review see, G. B. Sanders, J. M. Pot, and E. Havinga, *Fortschr. Chem. Org. Naturst.*, **27**, 129 (1969).

(4) E. J. Corey and A. G. Hortman, *J. Amer. Chem. Soc.*, **85**, 4033 (1963).

(5) E. Vogel, W. Grimme, and E. Dinne, *Tetrahedron Lett.*, 391 (1965).

(6) W. G. Dauben and M. S. Kellogg, *J. Amer. Chem. Soc.*, **93**, 3805 (1971).

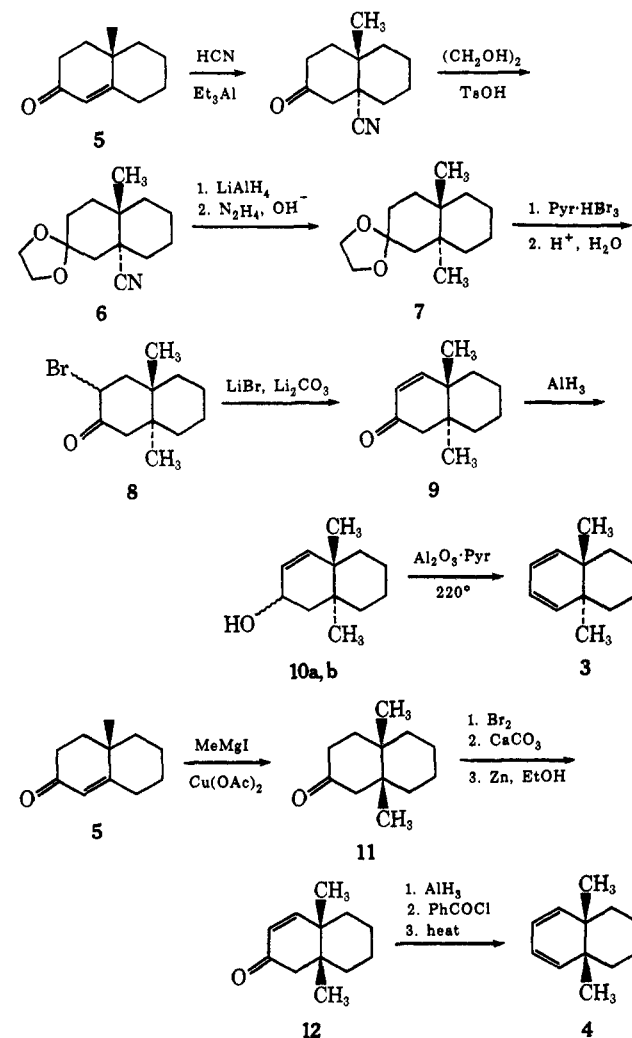
(7) W. G. Dauben, J. Rabinowitz, N. D. Vietmeyer, and P. H. Wendschuh, *ibid.*, **94**, 4285 (1972).

(8) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970; H. E. Zimmerman, *Angew. Chem., Int. Ed. Engl.*, **8**, 1 (1969); M. J. S. Dewar, *ibid.*, **10**, 761 (1971).

(9) We have chosen the decalin numbering system with the ring juncture positions being 9 and 10.

The syntheses of both *trans*- and *cis*-9,10-dimethyl- $\Delta^{1,3}$ -hexalin (**3** and **4**) proceeded as shown in Scheme I. Hydrocyanation of 10-methyl- $\Delta^{1,9}$ -octalin-2-one

Scheme I. Synthesis of *trans*- and *cis*-9,10-Dimethyl- $\Delta^{1,3}$ -hexalin



(**5**)¹⁰ with triethylaluminum catalysis¹¹ gave a 3:2

(10) N. C. Ross and R. Levine, *J. Org. Chem.*, **29**, 2341 (1964).

(11) W. Nagata, M. Yoshioka, and S. Hirai, *Tetrahedron Lett.*, 461 (1962).

mixture of *trans*- and *cis*-9-cyano-10-methyldecalin-2-one, respectively. The *trans* isomer was most conveniently separated by fractional crystallization of the ethylene ketals. The cyano group of the *trans* ketal **6** was reduced with lithium aluminum hydride to the imine, which was further reduced by the Wolff-Kishner process to *trans*-9,10-dimethyldecalin-2-one ethylene ketal (**7**). Bromination of **7** with pyridinium hydrobromide perbromide followed by hydrolysis of the ketal gave the bromo ketone **8**. This latter compound had a sharp melting point and was presumably one isomer. Dehydrobromination with lithium bromide and lithium carbonate gave enone **9**. Attempted reduction of this enone with lithium aluminum hydride gave considerable carbon-carbon bond reduction. However, it was found that aluminum hydride (lithium aluminum hydride and aluminum chloride)¹² selectively reduced the carbonyl group, giving a mixture of approximately equal amounts of α and β alcohols **10a,b** in 93% yield and only 2% of saturated ketone. The stereochemical assignment of the alcohols (see Experimental Section) was based on the downfield shift of the 9-methyl group in the nmr spectrum of the α isomer, where a 1,3-diaxial interaction with the hydroxyl would be expected.¹³ Pyrolysis at 220° of the mixture of alcohols with alumina treated with pyridine gave *trans*-9,10-dimethyl- $\Delta^{1,3}$ -hexalin (**3**).

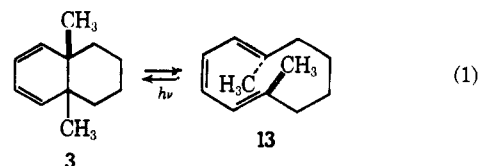
The synthesis of *cis*-9,10-dimethyl- $\Delta^{1,3}$ -hexalin (**4**), developed independently in these laboratories,¹⁴ was similar to that published by Marshall and coworkers.¹⁵ Thus, when the methyloctalone **5** was allowed to react with methylmagnesium iodide in the presence of cupric acetate, *cis*-9,10-dimethyldecalin-2-one (**11**) was produced, indicating predominant attack from the equatorial side. The melting point, 134–135°, was not in agreement with that of Marshall (108–118°), but the nmr and ir spectra compared well. Enol acetate formation on ketone **11** indicated that enolization occurred in both directions. Therefore, ketone **11** was treated with 2 mol of bromine and the crude dibromide was dehydrobrominated with calcium carbonate. The second bromine was removed with zinc in ethanol to give *cis*-9,10-dimethyl- Δ^2 -octalin-2-one (**12**). Aluminum hydride reduction gave the alcohol, the benzoate of which was pyrolyzed in refluxing *N,N*-dimethylaniline to give *cis*-9,10-dimethyl- $\Delta^{1,3}$ -hexalin (**4**).

The synthesis of the steroidal series proceeded along similar lines, and is detailed in the Experimental Section.

Results

Irradiation of a hexane solution of *trans*-9,10-dimethyl- $\Delta^{1,3}$ -hexalin (**3**) with a mercury resonance lamp rapidly established a photoequilibrium consisting of 46% diene and 54% of 1,6-dimethyl-*trans*-, *cis*-, *trans*-cyclodeca-1,3,5-triene (**13**). The triene **13** was isolated by silver nitrate extraction, and its nmr spectrum showed a six hydrogen singlet at δ 1.47 corresponding to the two methyl groups. The equivalence of the two methyl groups coupled with their

nonequivalence in the *cis*,*cis*,*trans* isomer (see below, **14**) indicates symmetry in **13**. The abnormally high

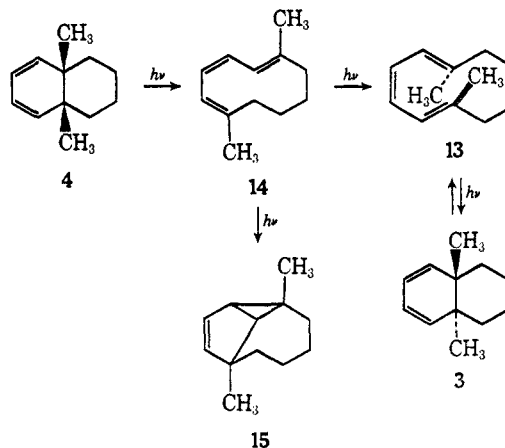


field position of these methyl groups derives from the transannular shielding by the opposing double bond and allows the assignment in **13** of *trans*,*cis*,*trans* instead of *cis*,*cis*,*cis* stereochemistry. The uv spectrum [uv max 262 nm (ϵ 1400), 214 (8150)] is indicative of a triene with poor overlap of the double bonds. Only after prolonged irradiation did other photoproducts begin to appear.

The same photochemical equilibrium was also obtained starting with triene. Thus, irradiation of 1,6-dimethyl-*trans*,*cis*,*trans*-cyclodeca-1,3,5-triene (**13**) under the same conditions rapidly gave *trans*-hexalin **3** as the only volatile photoproduct. The same 46% diene, 54% triene product ratio was established.

Irradiation of a pentane solution of *cis*-9,10-dimethyl- $\Delta^{1,3}$ -hexalin (**4**) with a medium-pressure mercury lamp gave a more complex mixture of photoproducts. Early in the irradiation 1,6-dimethyl-*cis*,*cis*,*trans*-cyclodeca-1,3,5-triene (**14**) was formed. As the irradiation continued, triene **14** was consumed while 2,7-dimethyltricyclo[5.3.0.0^{2,10}]dec-8-ene (**15**), triene **13**, and *trans*-hexalin **3** appeared. These secondary photoproducts are the compounds that would be expected from irradiation of the initially formed triene **14** and were isolated in 6, 15, and 22% yield, respectively. These results are summarized in Scheme II.

Scheme II. Photochemistry of *cis*-9,10-Dimethyl- $\Delta^{1,3}$ -hexalin



The photoproducts were separated by chromatography on silver nitrate impregnated silica gel. The nmr spectrum of triene **14** showed two methyl singlets at δ 1.64 and 1.71. If one assumes *cis* stereochemistry of the central double bond, then the only isomer which would have nonequivalent methyl groups is the *cis*,*cis*,*trans* isomer (**14**). The uv spectrum (uv max 262 nm (ϵ 6500)) showed considerably stronger absorption and thus indicates better overlap of the double bonds in this triene than in the *trans*,*cis*,*trans* isomer **13**.

The tricyclic photoproduct **15** showed methyl singlets in its nmr spectrum at δ 0.98 and 1.02 and a two

(12) M. J. Jorgenson, *Tetrahedron Lett.* 559 (1962).

(13) For a similar assignment, see G. Büchi, W. Hofheinz, and J. V. Paukstelis, *J. Amer. Chem. Soc.*, **91**, 6473 (1969).

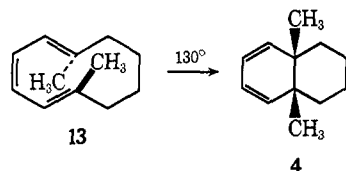
(14) R. G. Williams, Ph.D. Thesis, University of California, 1966.

(15) J. A. Marshall, W. I. Fanta, and H. Roebke, *J. Org. Chem.*, **31**, 1016 (1966).

proton vinyl absorption at δ 5.48. The uv spectrum (uv max 212 nm (ϵ 3700)) was characteristic of a cyclopropyl conjugated olefin.¹⁶ Hydrogenation gave a saturated dihydro derivative which showed no uv maximum above 180 nm and showed methyl singlets in its nmr spectrum at δ 0.90 and 1.05. This dihydro derivative was rapidly isomerized with hydrogen chloride in dry chloroform to give two new compounds with methyl adsorbances at δ 0.93 and 1.51, and at 1.40 and 1.53, thus confirming the presence of the cyclopropane ring.

The *trans,cis,trans* triene (13) from both irradiations gave identical ir and nmr spectra. Also, the *trans*-hexalin 3 from the second irradiation was identical in melting point, ir, and nmr with the synthetic material.

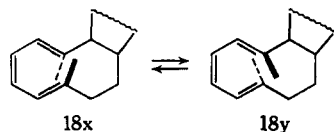
1,6-Dimethyl-*trans,cis,trans*-cyclodeca-1,3,5-triene (13) was found to undergo thermal conversion to *cis*-9,10-dimethyl- $\Delta^{1,3}$ -hexalin (4). A kinetic run was



made at 130° and the half-life for this reaction was found to be 60 min. First-order kinetics were obeyed throughout the reaction, which was run for 4 half-lives.

To further evaluate the substituent effect, the 5 α - and 5 β -methylandrosta-1,3-dien-17-ol acetates (16 and 17, respectively) were studied. The results were similar to those found in the hexalin series and are summarized in Scheme III. Thus, irradiation of the 5 α -methyl isomer led rapidly to a photostationary state consisting of two components (35 and 5%) in addition to starting material (60%). These materials were separated on silica gel impregnated with silver nitrate and purified by crystallization of their 17 β -ol derivatives, obtained by lithium aluminum hydride reduction. The first of these (18b) was shown by its spectral properties and uptake of 3 mol of hydrogen to be a triene. Based on analogy with the trienes obtained from *trans*- $\Delta^{1,3}$ -hexalins,⁴⁻⁶ this triene was assigned the *trans,cis,trans* stereochemistry.

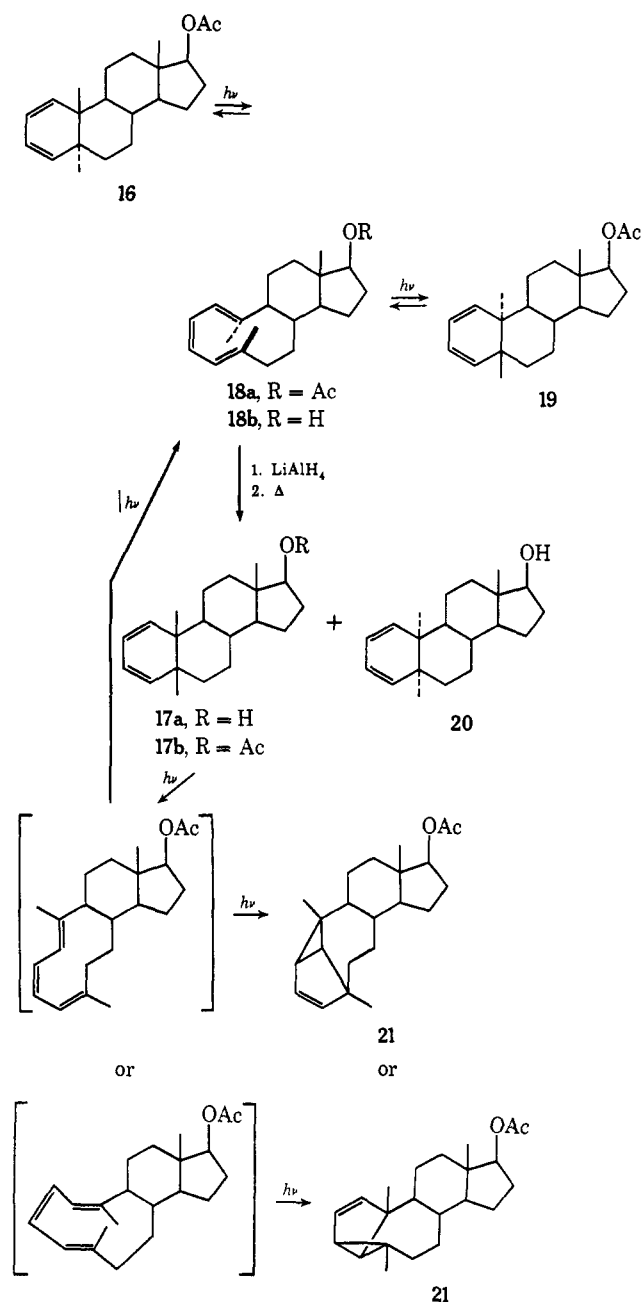
The nmr spectrum of this triene 18a showed an interesting temperature dependency. Cooling of the sample caused the signal for the C-19 methyl group to split into a doublet, while warming caused it to appear as a sharp singlet. The midpoint of the collapse occurred at 31° at 100 MHz, indicating a free energy of activation for the process of 16.5 kcal/mol. One possible explanation would be an interconversion of conformations 18x and 18y. That such a process



was not observed in the hexalin series is explained by the fact that the two analogous conformations would be mirror images. Triene 18b also exhibited a weak Cotton effect, which might be considered as additional

(16) J. Meinwald and R. S. Schneider, *J. Amer. Chem. Soc.*, **87**, 5218 (1965); J. Meinwald, A. Eckell, and K. L. Erickson, *ibid.*, **87**, 3532 (1965).

Scheme III. Photochemistry of 5 α - and 5 β -Methylandrosta-1,3-dien-17-ol Acetates (16 and 17b)



evidence for this interconversion, since the two conformations are of opposite helicity.

The second photoproduct from the irradiation was a diene isomeric with starting material and different from the 5 β -methyl compound 17. Of the remaining two possible isomers, 5 β -methyl-19 α -androsta-1,3-dien-17-ol acetate (19) is favored on the basis of a conrotatory photochemical closure of triene 18a. The same photoequilibrium was also obtained starting with triene acetate (18a).

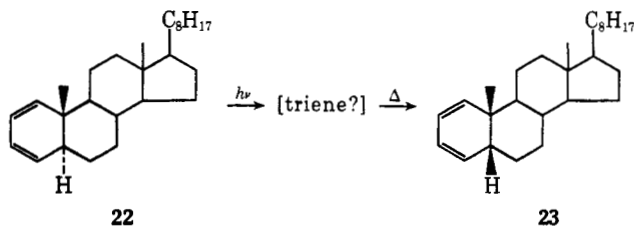
The triene alcohol 18b derived from 18a was found to undergo a thermal reaction with a half-life at 130° of 1 hr. A preparative run at 180° for 30 min in a sealed, evacuated tube gave two products, each in 9% yield. The first was the 5 β -methyl diene 17a, identical by infrared spectrum, melting point, and mixture melting point to the synthetic material. The second product was also a diene, as shown by its spectral

data. It was different from any other dienes encountered in the steroid series, and is assigned structure **20**, which has the only remaining A-B ring fusion. Both products are consistent with a disrotatory ring closure, which was the only observed thermal process in the hexalin series.

Irradiation of 5 β -methyl diene acetate **17b** gave the compounds found in the 5 α -methyl diene series and one additional product. The new product was assigned a vinylcyclopropane structure (**21**) on the basis of spectral properties and hydrogenation and treatment with hydrogen chloride, as in the hexalin series. It was not possible to choose between the two possible structures.

The new product is best explained on the basis of a trans,cis,cis triene precursor. In addition to triene **18**, another polar compound did appear on silver nitrate tlc in the early stages of the irradiation, but it never built up sufficiently for isolation.

In order to ascertain the effect of the methyl group at C-5, in this steroid series, 1,3-cholestadiene (**22**) was studied. Irradiation of **22** under similar conditions produced a mixture consisting only of starting material and a new product which could be isolated in 61% yield. The spectral data were consistent with an isomeric diene. Catalytic hydrogenation resulted in the uptake of 2 molar equiv of hydrogen and the product was identical in infrared spectrum, melting point, and mixture melting point with an authentic sample of 5 β -cholestane, indicating that the initial photoproduct was 5 β -1,3-cholestadiene (**23**).



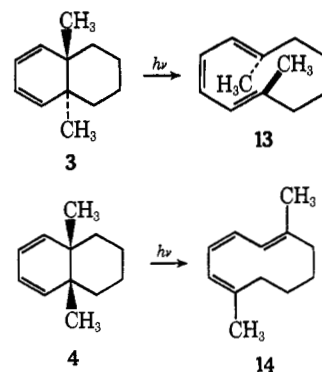
The product **23** is consistent with the formation of a trans,cis,trans triene, followed by a thermal closure of this triene to **23**. Attempts to detect such an intermediate at -35° by uv spectroscopy were unsuccessful, and the uv spectrum did not change on warming to room temperature, at which point approximately equal amounts of starting material and cis diene **23** were found.

Prolonged irradiation of **22** gave a triene assigned the trans,cis,cis stereochemistry and a vinylcyclopropane photoproduct analogous to **21**. The two products most likely are derived from the 5 β -H diene **23**.

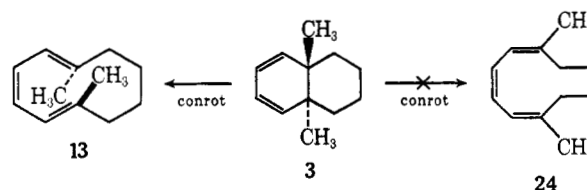
Discussion

The reactions observed in the steroid series were similar to those observed with the hexalins. Therefore, most of this section will deal with the hexalins and the generalization to the steroids should be obvious.

The first feature to note is the complete stereospecificity of the triene formation. *trans*-Hexalin **3** gave only trans,cis,trans triene **13**, while *cis*-hexalin **4** gave only the cis,cis,trans isomer **14** as the initially formed triene. These reactions are conrotatory in nature and are consistent with previous observations⁴⁻⁶ of the specificity of photochemical ring openings on which the orbital symmetry rules are based.⁸ *trans*-

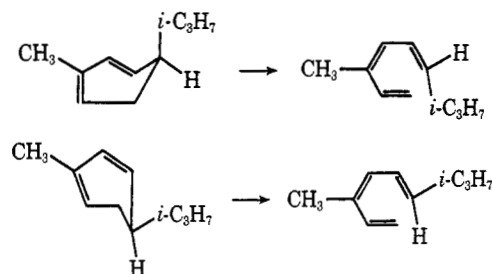


Hexalin **3** has two conrotatory modes of reaction available to it, one leading to cis,cis,cis triene **24** and the



other leading to trans,cis,trans triene **13**. Only the process leading to the more hindered triene **13** is observed.

This type of specificity has been encountered previously. Thus, Corey and Hortman got only opening in the same sense in their synthesis of dihydrocostunolide already mentioned.⁴ Baldwin and Krueger have observed specificity in the opening of the two conformations of α -phellandrene (**25**) in their temperature-dependent photochemical study.^{17a} The more

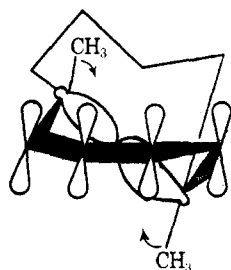


recent studies of Spangler and Hennis^{17b} also show that the favored process is the one in which the chirality of the nonplanar diene and the sense of the conrotatory opening are accordant.

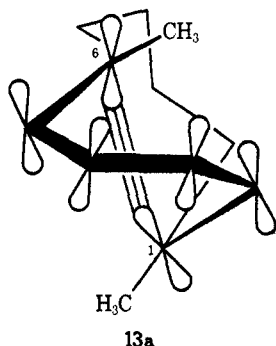
This observed process is that conrotatory mode in which maximum overlap of the developing p orbitals with the diene moiety is maintained. Conrotatory opening in the opposite sense would pass through a state where the developing p orbitals would be orthogonal to the diene moiety, and thus does not occur. The magnitude of this effect is striking, since rotation in the direction shown forces the bulky methyl groups toward the center of the ring and leads to the less stable triene.

Another striking feature of the photochemistry is the difference in products formed from the trans,cis,trans triene **13** and the cis,cis,trans triene **14**. Triene **13** photochemically closes very efficiently back to starting diene (eq 1), and only very slowly does it

(17) (a) J. E. Baldwin and S. M. Krueger, *J. Amer. Chem. Soc.*, **91**, 6444 (1969); (b) C. W. Spangler and R. P. Hennis, *J. Chem. Soc., Chem. Commun.*, 24 (1972).

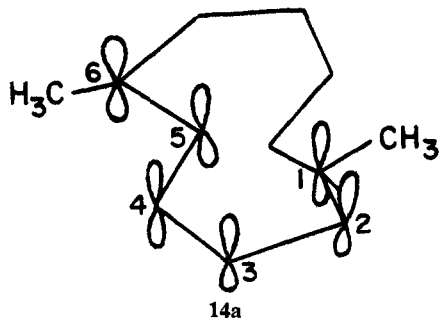


go on to additional products. This behavior can be explained on the basis of conformational control of reactivity. Triene **13** is very hindered, and the terminal methyl groups force the triene moiety into a helical form **13a**. This is shown by the uv spectrum



already mentioned and by molecular models. The proximity of orbitals 1 and 6 provides appreciable overlap in the excited state in the form of a Möbius array of six orbitals with one sign inversion.^{8b} Such a system would have aromatic character^{8b,c} leading to the observed closure to the diene product **3**. This is the same configuration that would be reached in the reaction of diene **3** to triene **13**, and thus both reactions are favored.

Contrastingly, *cis,cis,trans* triene **14** does not display such reactivity. Although such a closure may occur to a limited extent, the favored reactions are closure to tricyclic compound **15** and *cis-trans* isomerization of the terminal double bond, giving triene **13**. Although a conformation analogous to **13a** is possible for **14**, another conformation which is stabilized by greater planarity of the triene system and also minimized interaction of the methyl groups is available. This conformation (**14a**) puts orbitals 4 and 6 and



orbitals 1 and 5 in close proximity. The formation of the bicyclo[3.1.0]hexene **15** proceeds by a conrotatory cyclopropane ring closure of C-4 and C-6 followed by closure of C-1 and C-5 to form the five-membered ring.^{18,19} The most important feature here is the

(18) D. A. Seeley, *J. Amer. Chem. Soc.*, **94**, 4378 (1972).

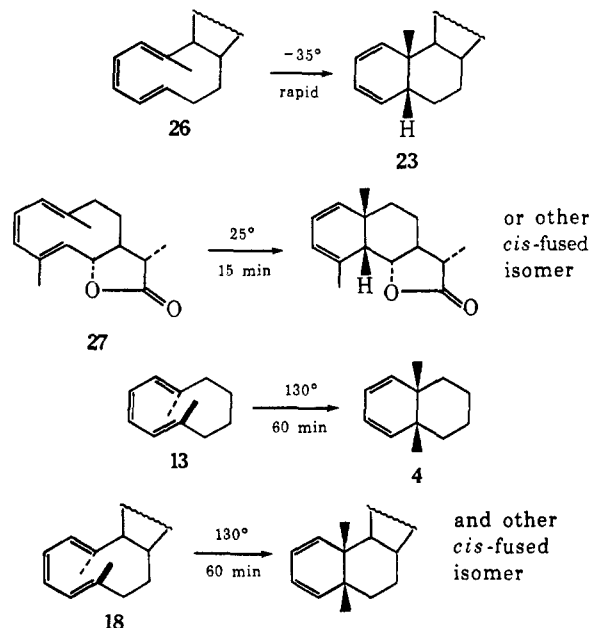
(19) (a) W. G. Dauben and M. S. Kellogg, *ibid.*, **94**, 8951 (1972);

(b) W. G. Dauben, M. S. Kellogg, J. I. Seeman, N. D. Vietmeyer, and P. H. Wendschuh, *Pure Appl. Chem.*, **33**, 197 (1973).

proximity of the orbitals. The reaction is not concerted^{19a} and can be visualized in terms of two basis sets; formally, the stereochemistry of the reaction is [$\pi 4_a + \pi 2_a$].

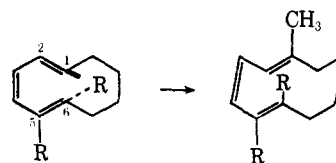
The thermal cyclization of the *trans,cis,trans* trienes also deserves comment (Scheme IV). Thus, the pro-

Scheme IV. Thermal Cyclizations of *Trans, cis,trans* Trienes

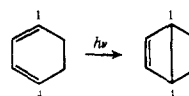


posed triene **26** in the cholestadiene photochemistry must close rapidly at -35° in order to escape detection. Triene **27** was reported⁴ to have a half-life for cyclization of 15 min at 25° . Trienes **13** and **18** closed with a half-life of 60 min at 130° . Thus with only one methyl group on the triene moiety, closure was not hindered. A second methyl group at the terminal atom of the triene system slowed the reaction dramatically, while a second methyl group at the next to the terminal atom had an intermediate effect.

The preferred conformations of the trienes is probably helical, and to get to the conformations required for closure to the *cis* dienes requires that either the substituent at C-1 (or C-6) or the substituent at C-2 (or C-5) must pass through the center of the ten-membered ring.



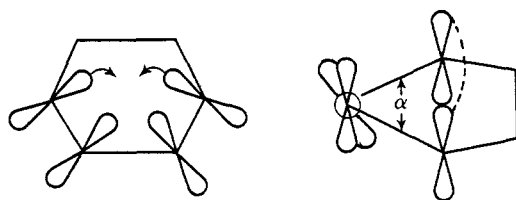
Finally, the fact that no diene closure to bicyclo[2.2.0]hexene type products, a common photochemical reaction in many systems,²⁰ was observed is of interest. This reaction involves bonding of orbitals 1 and 4 in the diene system



and thus requires close proximity of these atoms. The closures are disrotatory and these two features make the

(20) E. E. van Tamelen and S. P. Pappas, *J. Amer. Chem. Soc.*, **85**, 3297 (1963); J. B. Bremner and R. N. Warrener, *Chem. Commun.*, 926 (1967).

reaction proceed best when the four carbon atoms of the diene system are in one plane, *i.e.*, when the dihedral angle α between the two double bonds is zero. Indeed, systems which undergo this reaction



do have a dihedral angle of near zero.¹⁹ *trans*-Hexalin **3** has a very rigid ring fusion which locks the diene into a skewed conformation with a dihedral angle of *ca.* 20°. Although *cis*-hexalin **4** is more flexible, the planar conformation forces the two methyl groups into an eclipsed arrangement and therefore is not favored. Thus, the lack of such a reaction in this system lends support to the theory of ground state conformational control in the photochemistry of dienes.^{7,17}

Experimental Section

Ultraviolet spectra above 205 nm were recorded with a Perkin-Elmer 202 spectrophotometer, while those extending below 205 nm were run with a nitrogen-flushed Beckman DK2-A spectrophotometer. Nuclear magnetic resonance spectra were determined with tetramethylsilane as an internal standard and carbon tetrachloride as solvent unless otherwise stated. Hydrocarbon solvents for irradiations were purified with fuming sulfuric acid. Vpc runs were done on the following columns: (A) 1% Versamide 900 on 80–100 Gas Chrom Z, 5 ft $\times$ 0.25 in.; (B) 5% Carbowax 6000, 5% KOH on 60–80 Gas Chrom S, 10 ft $\times$ 1/8 in.; (C) 10% Carbowax 6000, 10% KOH on 60–80 Gas Chrom S, 5 ft $\times$ 0.25 in.; (D) 1% OV-1 on 100–120 Gas Chrom S, 15 ft $\times$ 1/8 in.; (E) 0.5% Versamide 900 on 100–120 Gas Chrom Z, 10 ft $\times$ 1/8 in.

All acetylations were done as follows: The 17-hydroxy steroid was dissolved in a mixture of pyridine (5 ml/g of steroid) and acetic anhydride (3 ml/g), and the solution was allowed to stand at room temperature overnight, poured onto ice, allowed to stand for 1 hr, and extracted with methylene chloride. The extracts were washed twice with hydrochloric acid (first with an amount of 12 *N* acid equal in volume to the pyridine and diluted threefold with water and ice, second with one-tenth this amount), once with saturated sodium bicarbonate, and once with saturated sodium chloride, dried (Na₂SO₄), and concentrated.

9-Cyano-10-methyl-2-decalones. The general method of Nagata, Yoshioka, and Hirai¹¹ was used. Thus, 123 ml (103 g, 0.905 mol) of triethylaluminum was added *via* syringe to 240 ml of ice cold, dry tetrahydrofuran (THF) under nitrogen and after 10 min, a solution of 26.6 ml (18.6 g, 0.69 mol) of anhydrous hydrogen cyanide²¹ in 150 ml of dry THF was added. After the mixture was stirred for 15 min, 60.5 g (0.37 mol) of 10-methyl- $\Delta^{1,9}$ -octal-2-one¹⁰ in 240 ml of THF and 2 ml of water was added and the mixture was stirred for 15 min at 0° and 4.5 hr at room temperature, poured slowly into a beaker containing 2 l. of ice and 1 l. of 15% sodium hydroxide, stirred for 30 min, and extracted thoroughly with ether. The combined extracts were washed twice with water, and then with 5% hydrochloric acid, 5% sodium carbonate, and saturated brine, dried and concentrated to give 62.7 g (89%) of slightly waxy, white solid. This crude product, which was a mixture of *cis* and *trans* isomers, was used in the next step.

***trans*-9-Cyano-10-methyl-2-decalone Ethylene Ketal (6).** A mixture of 65 ml of ethylene glycol, 300 ml of benzene, 250 mg of toluenesulfonic acid, and 62.7 g (0.327 mol) of crude *cis*- and *trans*-9-cyano-10-methyl-2-decalone was refluxed 19 hr with a Dean-Stark trap, at which time 8.5 ml (0.47 mol) of water had separated. The cooled mixture was washed with 5% sodium carbonate and with water, dried, concentrated, and recrystallized from ether-hexane to give 35.0 g (45.5%) of *trans*-9-cyano-10-methyl-2-decalone ethylene ketal: mp 111.5–112.5°; ir (CCl₄) 2230, 1140, 1115, 1085 cm⁻¹;

nmr δ 1.02 (s, 3, methyl), 1.1–2.2 (m, 14, aliph), and 3.69–4.16 (m, 4, ketal).

Anal. Calcd for C₁₄H₂₁NO₂: C, 71.45; H, 9.00; N, 5.95. Found: C, 71.48; H, 8.78; N, 6.00.

***trans*-9,10-Dimethyl-2-decalone Ethylene Ketal (7).** A solution of 33.0 g (0.14 mol) of *trans*-9-cyano-10-methyl-2-decalone ethylene ketal (6) in 200 ml of dry THF was added dropwise over a 40-min period to a stirred suspension of 6.1 g (0.16 mol) of lithium aluminum hydride in 100 ml of THF and the mixture was stirred for an additional 3.5 hr at room temperature. Water (6.1 ml) was added dropwise to the stirred mixture, followed by 18 ml of 15% potassium hydroxide and 6.0 ml of water. The mixture was filtered and concentrated to give 33.0 g of crude imine as a white solid. A mixture of 200 ml of triethylene glycol, 14.1 g (85%, 0.214 mol) of potassium hydroxide, and 16.6 ml (16.6 g, 0.332 mol) of hydrazine hydrate was added. The mixture was heated at 140° for 1 hr under nitrogen and the temperature was then gradually raised to 255° over a 2.5-hr period while 55 ml of a liquid distilled. The dark mixture was poured into water and extracted thoroughly with ether. The combined ether extracts were washed with water, dried, concentrated, and distilled through a 24-in. spinning band column to give 16.8 g (53.5%) of *trans*-9,10-dimethyl-2-decalone ethylene ketal: bp 61–63 (0.05 mm); ir (neat) 1095 cm⁻¹; nmr δ 1.05 (s, 3, methyl), 1.11 (s, 3, methyl), 1.15–2.20 (m, 14, aliph), and 3.60–4.05 (m, 4, ketal).

Anal. Calcd for C₁₄H₂₄O₂: C, 74.95; H, 10.78. Found: C, 75.14; H, 10.74.

3-Bromo-9,10-dimethyl-*trans*-decal-2-one (8). A solution of 20.8 g (0.065 mol) of pyridinium hydrobromide perbromide in 100 ml of dry THF was added rapidly to a stirred solution of 13.3 g (0.0595 mol) of *trans*-9,10-dimethyl-2-decalone ethylene ketal (7) in 100 ml of dry THF. The mixture was stirred for an additional 30 min and then made basic by the addition of aqueous sodium bicarbonate. Water was added and the mixture was extracted thoroughly with methylene chloride. The combined extracts were washed with water, dried, and concentrated to give the crude bromo ketal as a dark solid which still smelled of pyridine. This crude material was used in the next step.

A mixture of 25.3 g (at most 0.06 mol) of crude 3-bromo-9,10-dimethyl-*trans*-decal-2-one ethylene ketal, 100 ml of acetone, 45 ml of water, and 5.0 ml of sulfuric acid was refluxed for 1.25 hr, cooled to room temperature, and neutralized by the addition of a slurry of sodium bicarbonate. This mixture was diluted with water and extracted thoroughly with methylene chloride. The combined organic extracts were washed with water, dried, concentrated, and recrystallized from ether-hexane to give 7.8 g (51% for the two steps) of 3-bromo-9,10-*trans*-dimethyldecal-2-one (8); mp 131.5–132.0°; ir (CCl₄) 1735 cm⁻¹; nmr δ 0.98 (s, 3, methyl), 1.31 (s, 3, methyl), 1.10–2.00 (m, 10, aliph), 2.26 (AB q, 2, $\Delta\delta$ = 0.36, J = 14 Hz), and 4.70 (t, 1, J = 10 Hz).

Anal. Calcd for C₁₂H₁₈OBr: C, 55.61; H, 7.39; Br, 30.83. Found: C, 55.79; H, 7.26; Br, 30.6.

***trans*-9,10-Dimethyl- Δ^3 -octal-2-one (9).** A mixture of 4.1 g (0.047 mol) of lithium bromide, 5.5 g (0.074 mol) of lithium carbonate, and 30 ml of dry *N,N*-dimethylformamide (DMF) was stirred under nitrogen at 140° for 15 min. A solution of 7.5 g (0.029 mol) of bromo ketone 9 in 40 ml of DMF was added dropwise to the stirred mixture over a 20-min period, and the mixture was stirred at 140° for an additional 4 hr, cooled, poured into 15% acetic acid, and extracted thoroughly with methylene chloride. The combined extracts were washed thoroughly with water, dried, concentrated, and recrystallized from hexane to give 4.5 g (87%) of 9: mp 109–111°; uv max (hexane) 226 nm (ϵ 9100); ir (CCl₄) 1675 cm⁻¹; nmr δ 1.26 (s, 3, methyl), 1.10 (d, 3, J = 1 Hz), 2.18 (AB q, 2, $\Delta\delta$ = 0.49, J = 17 Hz), and 6.13 (AB q, 2, $\Delta\delta$ = 0.816, J = 10 Hz).

Anal. Calcd for C₁₂H₁₈O: C, 80.85; H, 10.18. Found: C, 81.12; H, 9.97.

3 β -Hydroxy- and 3 α -Hydroxy-9,10-*trans*-dimethyl- Δ^1 -octalin (10a and 10b). Aluminum chloride (203 mg, 1.52 mmol) was added to an ice cooled, stirred suspension of 182 mg (4.80 mmol) of lithium aluminum hydride in 50 ml of dry ether. The mixture was stirred under nitrogen for 10 min and allowed to warm to room temperature. A solution of 1.022 g (5.75 mmol) of *trans*-9,10-dimethyl- Δ^1 -octal-3-one (9) in 25 ml of dry ether was added and the mixture was stirred for 1 hr under nitrogen at room temperature. Aqueous 15% potassium hydroxide (1.15 ml) was added dropwise and after stirring for 10 min the mixture was dried, concentrated, and chromatographed on a 2.2 $\times$ 36 cm silica gel column slurry packed with 7.5% ether in hexane. Elution with 100-ml fractions of the same solvent gave the following: Fractions 6–8, 22 mg of

(21) K. Ziegler, "Organic Syntheses," Collect. Vol. I, Wiley, New York, N. Y., 1941, p 314.

saturated ketone identical by nmr with that obtained by hydrolysis of ketal **7**; Fractions 9–15, 499 mg of β -hydroxy-*trans*-9,10-dimethyl- Δ^1 -octalin (**10a**), mp 85–86°; Fractions 16–17, 48 mg of a mixture of α and β alcohols, and Fractions 18–27, 414 mg of α -hydroxy-*trans*-9,10-dimethyl- Δ^1 -octalin (**10b**), mp 64–65°, yield 961 mg (93%). The β alcohol had the following spectral properties: ir (CCl₄) 3390, 2924, 1468, 1445, 1036, 1008, 976, 962, 951, 923, and 877 cm⁻¹; nmr (CCl₄) δ 5.50 (s, 2, vinyl), 4.13 (br d, 1, CHOH, $J = 7$ Hz), 2.46 (s, 1, OH), 1.80–2.30 (m, 2, CH₂CHOH), 1.25–1.70 (m, 8, methylenes), 1.07 (s, 3, 9-methyl), and 0.97 (s, 3, 10-methyl). The α alcohol had the following spectral properties: ir (CCl₄) 3390, 2967, 2882, 1477, 1462, 1445, 1374, 1043, 1017, 956, and 943 cm⁻¹; nmr (CCl₄) δ 5.41 (s, 2, vinyl), 4.23 (br t, 1, CHOH, $J = 8$ Hz), 2.27 (s, 1, OH), 1.20–1.75 (m, 10, methylenes), 1.12 (s, 3, 10-methyl), and 1.00 (s, 3, 9-methyl).

Anal. Calcd for C₁₂H₂₀O: C, 79.94; H, 11.18. Found (β alcohol): C, 79.96; H, 11.20. Found (α alcohol): C, 79.83; H, 11.12.

trans-9,10-Dimethyl- $\Delta^{1,3}$ -hexalin (3). The method of Marshall, *et al.*,¹⁵ for dehydration of the corresponding *cis* alcohol was used. Thus, a mixture of 2.0 g of alumina containing 2% pyridine and 0.300 g (1.67 mmol) of a mixture of α -hydroxy- and β -hydroxy-*trans*-9,10-dimethyl- Δ^1 -octalin was heated at 240° for 1 hr while a stream of nitrogen swept the crude product into a Dry Ice trap. Bulb-to-bulb distillation at 60° (3 mm) gave 154 mg (57%) of *trans*-9,10-dimethyl- $\Delta^{1,3}$ -hexalin (**3**): mp 78–80°; uv max 264 nm (ϵ 2700); ir (CCl₄) 2940, 1712, 1647, 1471, 1445, 1160, 1017, and 978 cm⁻¹; nmr (CCl₄) δ 5.24–5.82 (m, 4, vinyl), 1.13–2.16 (m, 8, methylenes), and 1.05 (s, 6, methyls); m/e 162, 147, 119, and 105.

Anal. Calcd for C₁₂H₁₈: C, 88.82; H, 11.18. Found: C, 88.54; H, 10.92.

cis-9,10-Dimethyldecal-2-one (11). Methylmagnesium bromide solution was prepared as usual starting with 60 g (2.46 mol) of magnesium turnings and 1.5 l of dry THF. This solution was added to a stirred mixture of 4.84 g (0.0246 mol) of cupric acetate hemihydrate, 40 g (0.243 mol) of 10-methyl- $\Delta^{1,9}$ -octalin-2-one (**5**), and 2 l of THF under nitrogen at 0°. The solution was stirred for 1 hr, poured into a mixture of ice and dilute hydrochloric acid, and extracted thoroughly with methylene chloride. The organic phase was washed with water, saturated sodium bicarbonate, and saturated sodium chloride, dried (Na₂SO₄), and concentrated. The oily product was chromatographed on a column of 400 g of neutral Woelm alumina (Activity II). Elution with pentane gave a fraction of 25.7 g of an oil, followed by a fraction which could be crystallized from cold pentane to yield 9.61 g (22%) of the title compound **11**, mp 134–135°. Distillation of the former fraction under reduced pressure (to remove the diene resulting from 1,2 addition followed by elimination) left a residue which was recrystallized from cold pentane to yield an additional 6.23 g (14%) of product: mp 133–134°; ir (CCl₄) 1715 cm⁻¹; nmr δ 0.91 (s, 3), 1.04 (s, 3).

Anal. Calcd for C₁₂H₂₀O: C, 79.94; H, 11.18. Found: C, 79.70; H, 11.07.

cis-9,10-Dimethyl- Δ^3 -octal-2-one (12). To a stirred solution of 9.61 g (0.0531 mol) of ketone **11** in 100 ml of acetic acid was rapidly added a solution of 5.7 ml (17 g, 0.106 mol) of bromine and 20 microdrops of 48% hydrobromic acid in 25 ml of acetic acid. The reaction mixture was allowed to stand for 2 hr and diluted with water, and the aqueous solution was extracted with methylene chloride. The extracts were washed with water, saturated sodium bicarbonate, and saturated sodium chloride, dried (Na₂SO₄), and concentrated to yield 17.9 g (99.5%) of crude bromo ketone as an oil which later partially crystallized. The crude product was refluxed in 100 ml of DMF containing 10 g of calcium carbonate for 1 hr. Most of the solvent was distilled, and the residue was diluted with water and extracted thoroughly with methylene chloride. The extracts were washed successively with dilute hydrochloric acid, saturated sodium bicarbonate, and saturated sodium chloride, dried (Na₂SO₄), and concentrated. This residue was dissolved in 100 ml of absolute ethanol containing ca. 5 g of acid-washed zinc dust and the solution was refluxed under nitrogen for 10 hr. The excess zinc was filtered, and the filtrate was concentrated. The residue was dissolved in methylene chloride and washed with dilute hydrochloric acid, saturated sodium bicarbonate, and saturated sodium chloride, dried (Na₂SO₄), concentrated, and distilled, bp 100–110° (1.4 mm), to give 7.17 g (75%) of enone **12**: mp 73–77°; uv max (MeOH) 234 nm (ϵ 7050); ir (CCl₄) 1681 cm⁻¹; nmr δ 1.01, 1.08 (s, each 3), 1.50 (br, 8), 2.22 (s, 2), 5.76 (d, 1, $J = 10$ Hz), and 6.43 (d, 1, $J = 10$ Hz).

Anal. Calcd for C₁₂H₁₈O: C, 80.85; H, 10.18. Found: C, 80.57; H, 10.24.

cis-9,10-Dimethyl- $\Delta^{1,3}$ -hexalin (4). To a mixture of 1.8 g (0.047 mol) of lithium aluminum hydride in 150 ml of dry ether at 0° was added 1.97 g (0.0147 mol) of anhydrous aluminum chloride. The mixture was stirred for 15 min, and the precipitated salts were allowed to settle. The supernatant layer was carefully decanted, and 100 ml of the solution was added over 15 min to a solution of 6.99 g (0.0392 mol) of ketone **12** in 50 ml of dry ether at –50°. The solution was stirred under nitrogen for 30 min, 1 ml of water was added, and the solution was warmed to room temperature. An equal volume of dilute hydrochloric acid was added, and the ether layer was washed with saturated sodium bicarbonate and saturated sodium chloride, dried (Na₂SO₄), and concentrated to yield 7.03 g (99%) of the mixture of isomeric Δ^1 -3-ols. The crude product was dissolved in a cold solution of 100 ml of pyridine and 25 ml of benzoyl chloride and the mixture was allowed to stand overnight. An excess of glycine was added, whereupon the solution immediately warmed and turned very dark. The mixture was poured onto ice and extracted with methylene chloride. The organic layer was washed with dilute hydrochloric acid followed by dilute sodium hydroxide, concentrated, and chromatographed on 200 g of silica gel. The column was eluted with approximately 1 l. of pentane–5% ether to yield 10.45 g of benzoates as a light-yellow oil. The crude benzoate was dissolved in 100 ml of *N,N*-dimethylaniline and refluxed under nitrogen for 36 hr. The reaction mixture was poured into a cold mixture of 100 ml of concentrated hydrochloric acid and crushed ice and extracted with pentane. The extracts were washed with dilute hydrochloric acid, saturated sodium bicarbonate, and saturated sodium chloride, dried (Na₂SO₄), and concentrated to yield 5.57 g (88%) of a crude oil. The oil was chromatographed on 100 g of neutral Woelm alumina (Activity I). Elution with 150 ml of pentane gave 4.73 g (74.5%) of diene **4**: mp 35–38°; uv max (heptane) 262 nm (ϵ 3250); ir (CS₂) 755, 699 cm⁻¹; nmr δ 0.92 (s, 6), 1.38 (s, 8), 5.52 (br m, 4). These properties are in good agreement with the reported values.¹⁵

Anal. Calcd for C₁₂H₁₈: C, 88.82; H, 11.18. Found: C, 88.92; H, 10.95.

Preparative Irradiation of *trans*-9,10-Dimethyl- $\Delta^{1,3}$ -hexalin (3). A solution of 170 mg of *trans* diene **3** in 75 ml of purified hexane was irradiated with a mercury resonance lamp through quartz while nitrogen was bubbled through the solution. After 70 min a photostationary state was reached with 54% photoproduct and 46% starting material (determined by vpc analysis on column D). The photoproduct was selectively extracted with five 50-ml portions of 35% (w/v) aqueous silver nitrate. Concentrated ammonium hydroxide solution (120 ml) was added to the aqueous extracts and the cloudy mixture was extracted thoroughly with pentane. Concentration of the pentane solution gave 49 mg (52% recovery) of pure 1,6-dimethyl-*trans,cis,trans*-1,3,5-cyclodecatriene (**13**): uv max (heptane) 262 nm (ϵ 1400), 214 nm (ϵ 8150); ir (CCl₄) 2907, 1433, 1368, 938, 862, and 813 cm⁻¹; nmr (CCl₄) δ 5.95 (br s, 2, vinyl), 5.48 (br s, 2, vinyl), 1.50–2.30 (m, 8, methylenes), and 1.47 (s, 6, methyls).

Anal. Calcd for C₁₂H₁₈: C, 88.82; H, 11.18. Found: C, 89.02; H, 11.27.

Irradiation of 1,6-Dimethyl-*trans,cis,trans*-1,3,5-cyclodecatriene (13). A solution of 4 mg of triene in 2 ml of purified hexane was irradiated with a mercury resonance lamp through Vycor. After 43 min a photostationary state had been reached with 54% starting material and 46% of *trans*-9,10-dimethyl- $\Delta^{1,3}$ -hexalin (**3**), as determined by vpc analysis (column D). This is the same photostationary state obtained starting with the hexalin.

Pyrolysis of 1,6-Dimethyl-*trans,cis,trans*-1,3,5-cyclodecatriene (13). Aliquots (1 ml) of a solution of 3 mg of triene **13** and 15 mg of hexadecane (internal standard) in 50 ml of cyclohexane were sealed in Pyrex tubes and immersed in an oil bath at 130 (± 0.3)°. Samples were removed at 30, 60, 120, and 240 min and analyzed by vpc (column D). Triene **13** was converted cleanly into one product having identical vpc characteristics to *cis*-9,10-dimethyl- $\Delta^{1,3}$ -hexalin (**4**). No polymer was formed. First-order kinetics were observed with a half-life of 60 min.

Irradiation of *cis*-9,10-Dimethyl- $\Delta^{1,3}$ -hexalin (4). A solution of 0.600 g of diene **4** in 130 ml of pentane was irradiated with a Hanovia 200-W medium-pressure mercury lamp using a Vycor filter for 1 hr. The optical density at the maximum dropped very rapidly at first, but became nearly stationary at the end of 1 hr, after having reached 61% of its original value. Vpc (column B, 60°) showed products with retention times of 0.6, 1.2, 2.2, and 3.7 relative to starting material. The last of these peaks grew in initially, but had almost completely disappeared by the end of the irradiation, and corresponds to 1,6-dimethyl-*cis,cis,trans*-cyclodeca-1,3,5-triene (**14**).

The solution was concentrated under vacuum without heating and the pungent residue was chromatographed on a column of 18 g of silica gel-10% silver nitrate using 50-ml fractions; the first two fractions were pentane, the next two were pentane-10% ether, and the last was pentane-50% ether. Fraction 1 was rechromatographed on 5 g of silica gel-10% silver nitrate to yield 0.130 g (22%) of trans diene 3, mp 77-78°; identical uv, ir, and nmr spectra to the synthetic material.

Fraction 2 of the original chromatography gave 0.037 g (6%) of 2,7-dimethyltricyclo[5.3.0.0^{2,10}]dec-8-ene (15): uv max (heptane) 212 nm (ϵ 3700); ir (CS₂) 807, 756, and 741 cm⁻¹; nmr δ 0.98 (s, 3), 1.02 (s, 3), 1.1-1.8 (br, 10), 5.48 (t, 2, J = 1 Hz).

Anal. Calcd for C₁₂H₁₈: C, 88.82; H, 11.18. Found: C, 88.80; H, 11.08.

Combined fractions 4 and 5 of the original chromatography gave 0.104 g (17%) of a mixture of 13 and 14 in the ratio of 8:1, separated by preparative vpc. Compound 13 was identical by ir, nmr, and uv to the triene obtained from irradiation of trans diene 3. Purified compound 14 was a liquid: uv max (heptane) 262 nm (ϵ 6500), 212 (10,400); ir (CS₂) 1631, 720 cm⁻¹; nmr δ 1.64 (s, 3), 1.71 (s, 3), 5.7 (br, 4).

Anal. Calcd for C₁₂H₁₈: C, 88.82; H, 11.18. Found: C, 88.64; H, 11.08.

Degradation of Photoproduct 15. A solution of 62 mg (0.38 mmol) of photoproduct 15 in 5 ml of methanol was hydrogenated over 10 mg of platinum oxide at atmospheric pressure and room temperature. Hydrogen uptake ceased after 2 hr with a relative uptake of 1.03 mol. The mixture was filtered and concentrated to give 18 mg (29%) of a colorless oil, homogeneous to vpc; ϵ_{200} 730, ϵ_{180} 3100 (no max before 180 nm); infrared spectrum showed loss of the bands at 756 and 741 cm⁻¹, as well as those above 3000 cm⁻¹; nmr δ 0.90 (s, 3), 1.05 (s, 3); m/e 164.

The dihydro derivative (10 mg) was dissolved in 0.2 ml of dry chloroform in an nmr tube. The spectrum was run, and dry hydrogen chloride was bubbled through the solution for 1 min. The spectrum was rerun immediately. The peaks at δ 0.90 and 1.05 had completely disappeared. New, sharp singlets were present at δ 0.93, 1.04, 1.51, and 1.53, all of approximately equal intensity. A peak at 4.34 was also produced in a control run with just chloroform and HCl. No other peaks were present in the vinyl hydrogen region. After 2 hr standing, the peaks at 0.93 and 1.51 grew somewhat relative to the other two.

5 α -Cyanoandrostan-3-on-17 β -ol Ethylene Ketal (28). A vigorously stirred solution of 17.44 g (0.0552 mol) of 5 α -cyanoandrostan-3-on-17 β -ol,²² 100 ml of ethylene glycol, and 0.526 g of *p*-toluenesulfonic acid monohydrate in 1 l. of dry benzene was heated at a temperature just sufficient to maintain very slow distillation at a rate such that 500 ml of distillate was collected in 12 hr. Another 500 ml of dry benzene was added to the solution and distillation was continued until an additional 600 ml of distillate had been collected. To the hot, stirred solution was added ca. 5 g of solid sodium bicarbonate and the mixture was allowed to cool, diluted with 100 ml of saturated sodium bicarbonate solution, and extracted with methylene chloride. The extracts were processed in the usual manner, and concentrated under reduced pressure until precipitation began. The solution was allowed to cool and the precipitate was filtered. The mother liquor was concentrated to yield two additional crops and the total product was washed with benzene and air dried to yield 17.21 g (87.3%) of the ketal 28 as white needles: mp 260.5-261.5°; $[\alpha]_D^{25} +17.3^\circ$ (c 0.391); ir (CHCl₃) 2230 and 1080 cm⁻¹.

Anal. Calcd for C₂₂H₃₃O₃N: C, 73.50; H, 9.25; N, 3.90. Found: C, 73.35; H, 8.98; N, 4.05.

5 α -Methylandrostan-3-on-17 β -ol Acetate Ethylene Ketal (29). A solution of 15.73 g (0.0439 mol) of cyano ketal 28 in 350 ml of tetrahydrofuran was added at 0° to a stirred mixture of 9 g (0.237 mol) of lithium aluminum hydride in 400 ml of tetrahydrofuran. The solution was stirred for 3.5 hr at room temperature and cooled again to 0°. The excess lithium aluminum hydride was decomposed with water until hydrogen evolution ceased, followed by 20 ml of acetic acid. The solution was stirred for 1 hr and extracted with methylene chloride. The extracts were washed with water, with dilute sodium hydroxide until the washings were basic, and with water to neutrality, dried (Na₂SO₄), and concentrated to give 8.00 g of a crude oil showing in the infrared spectrum a strong band at 1710 cm⁻¹, characteristics of an aldehyde. The combined aqueous washings were neutralized with dilute sodium hydroxide

solution and extracted with methylene chloride. The extracts were washed with water, dried (Na₂SO₄), and concentrated to yield 5.57 g of crude material showing an infrared band at 1635 cm⁻¹, indicative of an imine. The crude mixture of products (13.57 g) was dissolved in 500 ml of diethylene glycol with 60 ml of 85% hydrazine hydrate and 25 g of solid potassium hydroxide. The mixture was stirred for 4 hr at 130°. The temperature was raised to 230-240° by distillation of water and hydrazine, and stirring was continued for 3 hr. The solution was cooled, poured onto ice, and extracted with methylene chloride. A portion of crystalline material which did not dissolve was filtered, washed with methylene chloride, and dried under vacuum to yield 4.04 g of crude hydroxy ketal. The combined methylene chloride extracts and washings were washed with water, dried (Na₂SO₄), and concentrated to 100 ml, during which considerable material precipitated. The mixture was heated on a steam bath for 15 min, cooled, and filtered. The product was washed with methylene chloride and dried under vacuum to yield an additional 5.97 g of crude hydroxy ketal. The combined portions of product were acetylated in the usual manner and the product was recrystallized from ethanol to yield 7.83 g (46%) of 29, mp 161-163°, $[\alpha]_D^{25} -12.0^\circ$ (c 0.467); ir (CCl₄) 1733 and 1088 cm⁻¹.

Anal. Calcd for C₂₄H₃₈O₄: C, 73.81; H, 9.81. Found: C, 73.66; H, 9.87.

2 α -Bromo-5 α -methylandrostan-3-on-17 β -ol Acetate Ethylene Ketal (30). To a stirred solution of 7.48 g (0.0191 mol) of ketal 29 in 70 ml of dry tetrahydrofuran was added, dropwise, a solution of 6.82 g (0.021 mol) of pyridinium hydrobromide perbromide in 20 ml of dry tetrahydrofuran. The solution was stirred for 10 min at room temperature and then 2 g of solid sodium bicarbonate was added, followed by 20 ml of saturated sodium bicarbonate solution, and 50 ml of water. The solution was extracted thoroughly with methylene chloride, and the extracts were combined, washed with saturated sodium bicarbonate and saturated sodium chloride, dried (Na₂SO₄), and concentrated. The residue was digested for 30 min with 150 ml of boiling acetone, allowed to cool, filtered, washed with acetone, and dried to give 6.84 g (76%) of bromo ketal 30: mp 224-226° dec; $[\alpha]_D^{25} -10.1$ (c 0.391); ir (CCl₄) 1740 and 1145 cm⁻¹.

Anal. Calcd for C₂₄H₃₇O₄Br: C, 61.40; H, 7.94; Br, 17.02. Found: C, 61.13; H, 7.80; Br, 17.11.

5 α -Methyl- Δ^1 -androsten-3-on-17 β -ol Acetate (31). A solution of 8.93 g (0.0190 mol) of bromoketal 30 in 300 ml of acetic acid, 75 ml of water, and 7.5 ml of sulfuric acid was heated to boiling over 20 min and refluxed for an additional 10 min. The solution was cooled, diluted with 1500 ml of ice-water, and extracted thoroughly with methylene chloride. The combined extracts were washed twice with saturated sodium bicarbonate and once with saturated sodium chloride, dried (Na₂SO₄), and concentrated. The crude product was dissolved in 150 ml of DMF containing 5 g of calcium carbonate, and the mixture was stirred under reflux for 2.5 hr. Most of the solvent was distilled, the solution was diluted with water and sufficient dilute hydrochloric acid to dissolve the calcium carbonate, and extracted with methylene chloride. The combined extracts were washed with saturated sodium bicarbonate and saturated sodium chloride, dried (Na₂SO₄), and concentrated to yield a yellow oil which was reacylated in the usual manner. The product was treated with decolorizing charcoal and chromatographed on a column of 200 g of neutral Woelm alumina (Activity III) eluted with 100-ml fractions; No. 1-3, pentane-2% ether; No. 4-9, pentane-5% ether; No. 10-15, pentane-25% ether. Fractions 8-15 were combined and recrystallized from aqueous methanol to yield 3.88 g (59%) of 31: mp 117-119°; $[\alpha]_D^{25} +64.6$ (c 0.446); uv max (EtOH) 235 nm (ϵ 9000); ir (CCl₄) 1740 and 1680 cm⁻¹; nmr δ 0.79, 1.08, 1.19, 1.98 (s, each 3, methyls), 2.53 (d, 1, J = 17 Hz), 5.72 (d, 1, J = 10 Hz), 6.93 (d, 1, J = 10 Hz).

Anal. Calcd for C₂₂H₃₂O₃: C, 76.70; H, 9.36. Found: C, 76.63; H, 9.41.

5 α -Methylandrosta-1,3-dien-17 β -ol (32). To a solution of 0.510 g (0.0134 mol) of lithium aluminum hydride in 150 ml of dry ether at 0° was added 0.581 g (0.00435 mol) of anhydrous aluminum chloride. The solution was allowed to warm to room temperature and was stirred for 30 min. The precipitated salts were allowed to settle, the supernatant layer was carefully decanted, and 100 ml of this solution was slowly added to a stirred solution of 2.00 g (5.8 mmol) of enone 31 in 50 ml of dry ether at -60° under nitrogen. The mixture was stirred for 45 min at -50 to -60°. Ethyl acetate was added (1 ml) followed by 1 ml of water, and the mixture was allowed to warm to room temperature. More water was added, and the ether layer was washed with water and saturated sodium chloride, dried (Na₂SO₄), and concentrated to yield

(22) A. Bowers, *J. Org. Chem.*, **26**, 2043 (1961).

1.96 g of a mixture of Δ^1 -3-ols as a glass. The crude product was dissolved in a mixture of 20 ml of pyridine and 5 ml of benzoyl chloride at 0° and the solution was allowed to stand overnight at this temperature. The mixture was processed in the usual manner to yield the crude benzoate mixture as a light-yellow oil containing some benzoyl chloride. This crude product was dissolved in 50 ml of *N,N*-dimethylaniline and refluxed for 50 hr under nitrogen. The solution was cooled and poured into a mixture of approximately 200 ml of ice and 35 ml of concentrated hydrochloric acid. The mixture was extracted with methylene chloride, the extracts were washed twice with dilute hydrochloric acid and once with saturated sodium bicarbonate and concentrated. The oily residue was dissolved in 100 ml of methanol containing 3 g of potassium hydroxide and refluxed for 3 hr, diluted with water, and extracted with methylene chloride. The extracts were washed with water, dried (Na_2SO_4), and concentrated. The crude product was chromatographed on a column of 60 g of neutral Woelm alumina (activity II), eluted with 50-ml fractions: No. 1-5, pentane-10% ether; No. 6-12, pentane-25% ether. Fractions 8-11 were combined and recrystallized from methanol to yield 0.557 g (33%) of the title compound (32): mp 178-180°; $[\alpha]_D^{25} -95.0^\circ$ (*c* 0.403); ir (CCl₄) 3620, 3450, 3020, 710, and 695 cm^{-1} ; uv max (MeOH) 266 nm (ϵ 3080); nmr (CDCl₃) δ 0.77 (s, 3), 1.06 (s, 6), 3.6 (m, 1), 5.8 (br m, 4).

Anal. Calcd for $\text{C}_{20}\text{H}_{30}\text{O}$: C, 83.86; H, 10.56. Found: C, 83.66; H, 10.47.

5 α -Methyl- Δ^1 -androstadien-17 β -ol Acetate (16). The diene 32 (0.557 g, 1.94 mmol) was acetylated in the usual manner. The product was recrystallized from methanol-ether to yield 0.569 g (89%) of 16: mp 129-130°; $[\alpha]_D^{25} -82.4^\circ$ (*c* 0.401); uv max (EtOH) 266 nm (ϵ 3200); ir (CS₂) 3010, 1733, 1656, 709, and 694 cm^{-1} ; nmr δ 0.77 (s, 3), 1.02 (s, 6), 1.93 (s, 3), 4.58 (m, 1), and 5.8 (br m, 4).

Anal. Calcd for $\text{C}_{22}\text{H}_{32}\text{O}_2$: C, 80.44; H, 9.82. Found: C, 80.70; H, 9.77.

5 β -Methylandrostan-3-on-17 β -ol Acetate (33). To a stirred mixture of 8.45 g (0.347 mol) of magnesium turnings in 1 l. of dry THF under nitrogen was added slowly through a calcium chloride tube methyl bromide by condensing on a Dry Ice condenser until all of the magnesium turnings had dissolved. The solution was cooled below 0° in an ice-salt bath and a solution of 10 g (0.0347 mol) of testosterone and 1.38 g (0.0069 mol) of cupric acetate monohydrate in 200 ml of THF was slowly added. The solution was allowed to warm to room temperature with stirring for 1 hr, worked up in the usual manner, and the residual oil acetylated. The crude product was chromatographed on neutral Woelm alumina and then eluted with pentane-50% ether. The material obtained was recrystallized from hexane to give 1.30 g (11.2%) of ketone (33): mp 157-159°; $[\alpha]_D^{25} +18.4^\circ$ (*c* 0.390); ir (CCl₄) 1740 and 1720 cm^{-1} ; nmr δ 0.78, 0.87, 0.92, 1.97 (s, each 3), 2.93 (d, 1, *J* = 14 Hz), and 4.57 (m, 1).

5 β -Methyl- Δ^1 -androst-3-on-17 β -ol Acetate (34). To a stirred solution of 4.58 g (0.0133 mol) of ketone 33 in 50 ml of acetic acid was added a solution of 1.41 ml (0.026 mol) of bromine and 5 drops of 48% hydrobromic acid in 10 ml of acetic acid. The solution was allowed to stand for 12 hr and diluted with water. The precipitated product was filtered, washed with water and with methanol, and air dried to yield 6.69 g of crude dibromide. The crude product was dissolved in 100 ml of boiling DMF containing 5 g of calcium carbonate and the solution was refluxed for 1 hr. Most of the solvent was distilled and the residue was diluted with water and extracted with methylene chloride. The extracts were washed with dilute hydrochloric acid, saturated sodium bicarbonate, and saturated sodium chloride. The solution was passed through a column of 50 g of neutral Woelm alumina (Activity II), and the column was eluted with additional methylene chloride until no further material was obtained. Concentration gave 4.65 of crude bromo enones. The crude product was dissolved in 50 ml of absolute ethanol. Acid-washed zinc dust (5 g) was added and the solution was stirred under reflux for 48 hr. The mixture was filtered and concentrated. The residue was acetylated in the usual manner. The resulting yellow oil was chromatographed on a column of neutral Woelm alumina (Activity II), and the crude product recrystallized from hexane to yield 1.521 g (35%) of enone 34, mp 110-112°. The analytical sample was prepared by rechromatography of a small sample and gave the following properties: mp 117-119°; $[\alpha]_D^{25} +107^\circ$ (*c* 0.4); ir (CCl₄) 3025, 1735, 1685, 1610 cm^{-1} ; uv max (EtOH) 236 nm (ϵ 8250); nmr δ 0.77, 0.91, 1.08, 1.94 (s, each 3), 2.97 (br d, 1, *J* = 16 Hz), 4.52 (m, 1), 5.76 (d, *J* = 10 Hz), 6.54 (d, 1, *J* = 10 Hz).

Anal. Calcd for $\text{C}_{22}\text{H}_{32}\text{O}_2$: C, 76.70; H, 9.36. Found: C, 76.61; H, 9.28.

5 β -Methylandrosta-1,3-dien-17 β -ol Acetate (17). Following the method used to prepare the 5 α diene 32, 1.58 g of enone 34 was converted to the crude 5 β -methyl diene. The mixture was sublimed at 120° (1 mm), acetylated in the usual manner, and chromatographed on neutral Woelm alumina (Activity II), and the product recrystallized from aqueous methanol to yield 0.710 g (47%) of the title compound 17: mp 83.5-84.5°; $[\alpha]_D^{25} +326.3^\circ$ (*c* 0.399); uv max (EtOH) 265 nm (ϵ 3150); ir (CS₂) 3040, 3020, 1735, 729, 691 cm^{-1} ; nmr δ 0.73, 0.80, 0.98, 1.92 (s, each 3), 4.50 (m, 1), and 5.53 (br m, 4); ORD $[\phi]_{400} +3650^\circ$, $[\phi]_{287} +48,800^\circ$, $[\phi]_{240} -62,400^\circ$, $[\phi]_{200} -58,500^\circ$ (*c* 0.0090, heptane).

Anal. Calcd for $\text{C}_{22}\text{H}_{32}\text{O}_2$: C, 80.44; H, 9.82. Found: C, 80.56; H, 9.73.

5 β -Methylandrosta-1,3-dien-17 β -ol (35). A small sample of diene acetate 17 was hydrolyzed in 5% methanolic potassium hydroxide for 2 days at room temperature. The sublimed product 35 had the following properties: mp 127-129°; $[\alpha]_D^{25} +250.8^\circ$ (*c* 0.093); ir (CS₂) 3580, 3320, 728, and 690 cm^{-1} ; nmr δ 0.68, 0.81, 1.01 (s, each 3), 1.97 (s, 1), 3.49 (m, 1), 5.53 (br m, 4).

Anal. Calcd for $\text{C}_{20}\text{H}_{30}\text{O}$: C, 83.86; H, 10.56. Found: C, 83.81; H, 10.37.

Irradiation of 5 α -Methylandrosta-1,3-dien-17 β -ol Acetate (16). The diene 16 (400 mg, 1.21 mmol) was dissolved in 130 ml of pentane and irradiated in the usual apparatus, with a Hanovia 200-W lamp and Vycor filter for 2 hr. The pentane solution was concentrated (without heating) and chromatographed on a column of 10 g of silica gel-silver nitrate eluted with 50 ml of pentane-5% ether followed by 50 ml of pentane-10% ether. The combined fractions were evaporated under reduced pressure to yield 270 mg which was recrystallized from methanol to yield 179 mg (45%) of recovered starting material, proved by identity of infrared spectrum and mixture melting point. The mother liquor was evaporated to yield an oil which was dissolved in 1 ml of ether, and there was added approximately 5 mg of lithium aluminum hydride. The solution was stirred, and minute quantities of water were carefully added until no further hydrogen evolution occurred. The salts were removed by centrifugation and washed with ether, and the combined organic solutions were evaporated. The residue was recrystallized from aqueous methanol to yield a very small fraction of the deacetylated derivative of photoproduct 19 still contaminated with 12% of deacetylated starting diene 16 and 8% other impurities (vpc): mp 120-137°; uv max 265 nm (ϵ 2100); ir (CS₂) 705 cm^{-1} ; nmr δ 0.74, 1.07, 1.26, (s, each 3), 3.55 (m, 1), and 5.6 (br m, 4); ORD $[\phi]_{450} +700^\circ$, $[\phi]_{285} +12,700^\circ$, $[\phi]_{242} -14,400^\circ$; $[\phi]_{220} -7600^\circ$ (*c* 0.0090, heptane); *m/e* 286.

The silver nitrate column was further eluted with ether until no more material was obtained to give 110 mg (27%) of triene acetate 18a as an oil which was not stable to the vpc conditions, and showed the following spectra: ir (CS₂) 1736, 1639, 979, 876, 820, 751, 698, 686 cm^{-1} ; nmr δ 0.82 (br s, 3), 4.56 (m, 1), 5.47 (broad, 2), and 6.05 (br, 2).

The 110 mg of triene acetate 18a was dissolved in 2 ml of ether, reduced to the alcohol with lithium aluminum hydride as above, and recrystallized from aqueous methanol to give white crystals of the corresponding alcohol 18b; mp 116-117°; $[\alpha]_D^{25} -11^\circ$ (*c* 0.10); uv (MeOH) 255 nm (sh, ϵ 1500), 210 sh (9300); ir (CS₂) 1645, 876, 823, 752, 698, 687 cm^{-1} ; ORD $[\phi]_{450} -120^\circ$, $[\phi]_{302} -2000^\circ$, $[\phi]_{248} +5300^\circ$, $[\phi]_{245} +5100^\circ$, $[\phi]_{221} +16,000^\circ$, $[\phi]_{210} +10,000^\circ$ (*c* 0.0182).

Hydrogenation of Photoproduct 19. A sample of the diene 19 (7.5 mg) in 1 ml of methanol with approximately 0.5 mg of platinum oxide was agitated under an atmosphere of hydrogen for 8 hr. The platinum was removed by centrifugation, and the methanol was evaporated. The product was recrystallized four times from aqueous methanol to yield a tetrahydro derivative, homogeneous to vpc, mp 132.0-133.5°, *m/e* 332.

Hydrogenation of the Deacetylated Derivative 18b of Phototriene 18a. A sample of triene was hydrogenated as above. The mass spectrum of the product indicated an uptake of 3 mol equiv of hydrogen.

Pyrolysis of the Phototriene Alcohol (18b). The triene (53 mg, 0.185 mmol) was sealed in an evacuated Pyrex tube and heated at 180° for 30 min. The product was fractionally recrystallized from methanol-water. The initial fractions gave approximately 5 mg (9%) of diene 20: mp 155-158°; $[\alpha]_D^{25} +118^\circ$ (*c* 0.100); uv max (heptane) 265 nm (ϵ 3000); ir (CS₂) 705, 690 cm^{-1} ; nmr (CDCl₃) δ 0.78, 0.87, 1.04 (s, each 3), 3.66 (m, 1), 5.6 (br m, 4); ORD $[\phi]_{450}$

+809°. [ϕ]₅₈₇ +25,000°; [ϕ]₂₄₁ -34,400°, [ϕ]₂₂₅ -28,000°, [ϕ]₂₁₀ -36,400°; *m/e* 286.

The latter fractions of the crystallization gave approximately 5 mg (9%) of diene 17a, mp 122–125°, identical in infrared spectrum and undepressed in mixture melting point with authentic diene 17a.

Irradiation of Phototriene 18a. A sample of the triene 18a (15 mg) was irradiated in 130 ml of pentane solution with the 200-W Hanovia lamp for 1 hr. The vpc trace at the end of this time was similar to that observed in irradiations starting with diene 16. Infrared spectrum confirmed the presence of diene 16 in the product.

Irradiation of 5 β -Methyl- $\Delta^{1,3}$ -androstadien-17 β -ol Acetate (17b). The diene 17b (300 mg, 0.915 mmol) was dissolved in 750 ml of pentane and irradiated with the 200-W Hanovia lamp and Vycor filter for 2 hr, at which time the optical density at the maximum had dropped 64%. The vpc trace showed the same pattern as was observed in the irradiation of the 5 α isomer 16 except that a new peak of relative retention time 0.57 now accounted for approximately 40% of the total area. The solvent was evaporated under reduced pressure, and the residual material was chromatographed on a column of 30 g of silica gel–silver nitrate. At the top of the column was packed approximately 1 cm of water-deactivated silica gel, since this was found to reduce blackening of the top of the silver-impregnated column. The column was eluted with 15-ml fractions: No. 1–17, pentane–3% ether; No. 18–19, pentane–10% ether; No. 20–25, pentane–20% ether; No. 26–29, pentane–30% ether. Fractions 10–13 were combined and recrystallized twice from methanol to yield 50 mg (17%) of material, mp 129–130°, identical in infrared spectrum and undepressed in mixture melting point with authentic 5 α diene 16. The mother liquors from above were concentrated and added to fractions 14–19 and the mixture was repeatedly rechromatographed on a column of 2 g of silica gel–silver nitrate. The column was eluted with pentane–3% ether and on each passage through the column the first few milligrams of material was discarded. After several cycles, there was obtained a fraction of material which could be fractionally recrystallized from methanol to yield 46.5 mg (15.5%) of vinylcyclopropane product 21: mp 65–66°; uv max (heptane) 221 nm (ϵ 3900); ir (CS₂) 3035, 3005, 1735, 769, 751 cm⁻¹ (in CCl₄ a very weak peak could be seen at 1597 cm⁻¹); nmr δ 0.82 (s, 3), 0.98 (s, 6), 1.94 (s, 3), 4.50 (m, 1), and 5.40 (wide s, 2); *m/e* 328.

Anal. Calcd for C₂₃H₃₂O₂: C, 80.44; H, 9.82. Found: C, 80.09; H, 9.80.

Fractions 22–24 of the original chromatography gave 18 mg (6%) of an uncharacterized oil. Fractions 26–29 of the original chromatography gave 83 mg (27%) of crude material which was reduced to the 17 β alcohol by the standard procedure. The product was recrystallized several times from methanol to give a sample, mp 94–99°, which was identical in infrared spectrum and vpc behavior with authentic triene obtained from the hydrolysis of triene 18.

Degradation of Photoproduct 21. A 10-mg sample of the photoproduct 21 was hydrogenated in methanol with a platinum catalyst. Vpc analysis showed only one product and no trace of starting material. The material had lost the infrared bands in the 700–800-cm⁻¹ region, confirming that the double bond had been reduced. The ultraviolet spectrum (pentane) showed no maximum above 180 nm but had an extinction coefficient of 1700 at 200 nm. The molecular weight was 330 (mass spectrum), which showed that only 1 mol of hydrogen was added. The crude dihydro photoproduct was dissolved in 0.5 ml of dry chloroform, and the solution was saturated with hydrogen chloride gas, allowed to stand for 1 hr, the solvent was evaporated under a stream of nitrogen, and the residue was dried under vacuum. The crude product showed the following spectra: uv max (pentane) 197 nm (ϵ 4300); ir (CS₂) 756 cm⁻¹. These results confirm the presence of a vinylcyclopropane moiety in photoproduct 21.

1,3-Cholestadiene (22). A solution of 12.4 g (0.0308 mol) of

3 β -chloro- Δ^1 -cholestene²³ and 25 ml of pyridine in 600 ml of DMF was refluxed overnight under nitrogen. The reaction mixture was worked up in the standard way and the residual oil chromatographed on 300 g of neutral Woelm alumina (Activity I). The column was eluted with 50-ml fractions of pentane. Fractions 7–9 gave 6.03 g of material which was recrystallized from methanol–ether to give 5.37 g (45%) of 1,3-cholestadiene (22): mp 60–61° (lit.²⁴ 67–68°); [α]_D²⁵ +78.2° (c 1.89); uv max (hexane) 262 nm (ϵ 3500); ir (CS₂) 3010, 736, and 699 cm⁻¹; nmr δ 5.3–5.9 (complex m, 4, vinyl), 0.92 (s, 3, C-19), 0.66 (s, 3, C-18); ORD [ϕ]₄₃₀ +230°, [ϕ]₃₅₀ +635°, [ϕ]₂₈₄ -1270°, [ϕ]₂₃₈ +6250, [ϕ]₂₁₀ +9450 (c 0.0086, heptane).

Anal. Calcd for C₂₇H₄₄: C, 87.97; H, 12.03. Found: C, 87.70; H, 11.86.

Irradiation of 1,3-Cholestadiene (22). A solution of 475 mg (1.29 mmol) of diene 22 in 130 ml of hexane was irradiated with an unfiltered 100-W medium-pressure Hanovia mercury lamp. Optical density of the solution dropped quite rapidly during the first 10 min of irradiation and considerably more slowly after this time. An isosbestic point occurred at 241 nm in the ultraviolet spectrum. Irradiation was stopped after 40 min, at which time the maximum had shifted to 266 nm and the extinction had dropped 16%. The solvent was evaporated under reduced pressure at room temperature to yield a light-yellow oil which showed only two peaks on vpc (column A, 218°); starting material (about 5%) and a product of relative retention time 0.81. The mixture was chromatographed on a column of 25 g of neutral Woelm alumina (Activity I) eluted with 6-ml fractions of pentane. The combined fractions 6–9 gave 290 mg (61%) of 5 β -1,3-cholestadiene 23 which did not crystallize: [α]_D²⁵ +120.0 (c 2.08); uv max 266 nm (ϵ 3000); ir (CS₂) 757 and 717 cm⁻¹; nmr δ 5.2–5.9 (m, 4, vinyl), 1.10 (s, 3, C-19), 0.66 (s, 3, C-18); ORD [ϕ]₄₃₀ +920, [ϕ]₃₅₄ +16,200°, [ϕ]₂₄₀ -20,800°, [ϕ]₂₁₁ -22,400° (c 0.010, heptane).

Hydrogenation of 5 β -1,3-Cholestadiene (23). The diene 23 (142 mg, 0.385 mmol) was hydrogenated at atmospheric pressure and room temperature in 50 ml of ethanol–5% dioxane with 12 mg of pre-reduced platinum oxide catalyst. Hydrogen uptake ceased after 3 hr with uptake of 2.2 mol equiv. The concentrated reaction product crystallized upon standing and was recrystallized from ether–ether to give 105 mg (73%) of 5 β -cholestane, mp 70–71°. The melting point was undepressed upon admixture with authentic 5 β -cholestane and the infrared spectra were superimposable.

Extended Irradiation of 1,3-Cholestadiene (22). The diene 22 (215 mg, 0.585 mmol) was dissolved in 130 ml of pentane and irradiated with an unfiltered 200-W Hanovia medium-pressure mercury lamp, for 20 min and concentrated (without heating). The residue was chromatographed on a column of 6 g of silica gel–silver nitrate, eluted with 5-ml fractions: No. 1–3, pentane; No. 4–9, pentane–3% ether; and No. 10–13, pentane–10% ether. Fractions 1–3 gave 10 mg (4.7%) of a vinylcyclopropane photoproduct as an oil, homogeneous to vpc (column A, 218°) with a relative retention time of 0.77; uv max (heptane) 208 nm (sh, ϵ 390); ir (CS₂) 776 and 757 cm⁻¹; nmr δ 5.41 (m, 2, vinyl), 1.03 (s, 3, C-19), 0.66 (s, C-18). Fractions of 5–7 gave 151 mg (70%) of 5 β -1,3-cholestadiene (23) containing a small amount of starting material. Fractions 12–13 yielded 31 mg (14%) of an oil whose structure is assigned trans,cis,cis triene analogous to 14 on the basis of the following spectral properties: uv max (heptane) 212 nm (ϵ 8700, 278 (1400)); ir (CS₂) 977, 812, 772, and 704 cm⁻¹; nmr δ 5.3–5.8 (m, 5, vinyl), 1.67 (br, s, 3, C-19), 1.30 (s, 3, C-18); ORD [ϕ]₄₃₀ +480°, [ϕ]₃₁₆ +13,600°, [ϕ]₂₃₇ -126,000°, [ϕ]₂₂₂ -219,000°, [ϕ]₂₀₅ +106,500° (c 0.0091, heptane).

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