Swain and Morgan[36] modified by Peterson.[37] Rates were done by this technique on tosylate ester concentrations ranging from 0.0015 to 0.40 *M*. The usual ampoule technique, using 5-ml aliquots, was employed.[38] The samples were quenched by delivering the aliquot into 95% ethanol. The absorbance of the ethanol solutions was measured at the sharp maximum at 272.5 mμ on a Cary Model 14M recording spectrophotometer. The quenched solutions were quite stable and no significant change in absorbance was found, after 1 hr, in most cases.

It was always necessary to dilute the trifluoroacetic acid sample prior to analysis (at least 0.5 ml of EtOH/5 ml of sample), the reason being that alkyl tosylates and tosylic acid not only have the same absorption maximum but also approximately the same extinction coefficient. When the sample contained less than 50% ethanol it was necessary to measure the absorbance immediately after the addition of the ethanol for the absorbance was found to decrease on standing, especially for the infinity point.

The extinction coefficient of 2-phenylethyl *p*-toluenesulfonate in 8% trifluoroacetic acid in 95% ethanol was 513. The infinity absorbances due to toluenesulfonic acid or sodium toluenesulfonate usually fell in the range 0.180–0.240, corresponding to a molar extinction coefficient of 125.

For the trifluoroacetolyses containing high concentrations of tetra-*n*-butylammonium tosylate, it was not possible to watch disappearance of the absorption of the ROTs for it was swamped by the absorption of the added tosylate salt. For concentrations of tetra-*n*-butylammonium tosylate greater than 0.1 *M*, it became necessary to extract the ROTs from the trifluoroacetic acid solution between pentane and water.[38] The pentane layer was evaporated to dryness and the residue was dissolved in 95% ethanol and then analyzed.

Nmr Studies in Trifluoroacetic Acid. Product studies and deuterium scrambling rates were performed in a sealed tube using *ca.* 0.4 ml of a 0.40 *M* solution of tosylate ester. The nmr tube was immersed in a constant temperature bath. At appropriate intervals it was withdrawn and cooled in ice and the nmr spectrum was recorded and integrated on an A-60 D Varian nmr spectrometer. The deuterium scrambling of 2-phenylethyl-*1,1-d*$_2$ tosylate was followed by measuring the decrease of the area of combined β proton signals in the ROTs (δ 2.55 ppm) and the $ROCOF_3$ (δ 2.67 ppm) from two protons to one.

(36) C. G. Swain and C. R. Morgan, *J. Org. Chem.*, **29**, 2097 (1964)
(37) P. E. Peterson, R. E. Kelley, Jr., R. Belloli, and K. A. Sipp *J. Amer. Chem. Soc.*, **87**, 5169 (1965).
(38) A. H. Fainberg and S. Winstein *ibid.*, **78**, 2770 (1956).

Synthesis of the Tetracyclo[11.1.0.0^{3,5}.0^{7,9}]tetradecan-11-ols. Possible Heptahomotropylium Ion Precursors[1]

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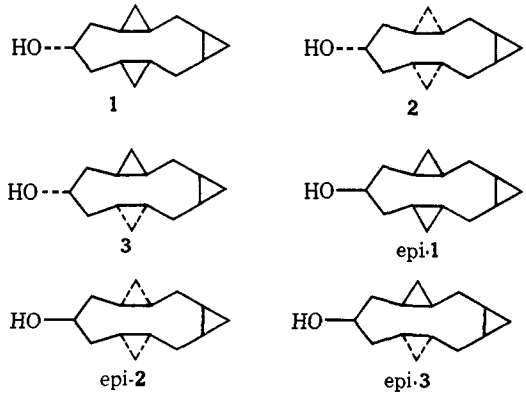
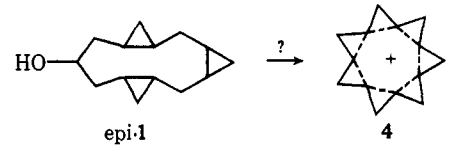
Abstract: The all-syn form of tetracyclo[11.1.0.0^{3,5}.0^{7,9}]tetradecan-11-ol, epi-**2**, has been synthesized by a route which utilizes a sequence of highly selective homoallylic ring expansions. Variations in the sequence allow synthesis of six related isomers and their corresponding ketones which were necessary for the structural assignment. The tosylate of epi-**1** is of interest as a possible precursor of the heptahomotropylium ion, **4**.

The present paper describes the synthesis of six previously unknown tetracyclo[11.1.0.0^{3,5}.0^{7,9}]tetradecan-11-ols, **1**, **2**, and **3**, and their epimers. The compounds are of considerable interest since epi-**1** is a possible precursor or heptahomotropylium ion, **4**. The primary synthetic goal was to obtain compound epi-**1**, but since it was totally unknown the other related compounds were necessary for spectral comparison. Accordingly, a route was devised which allowed modifications such that all six isomeric alcohols and their corresponding ketones could be obtained. The success of the scheme depends on three important observations which we have reported earlier.[4] The Simmons–Smith (SS) reactions[5] of medium sized ring allylic alco-

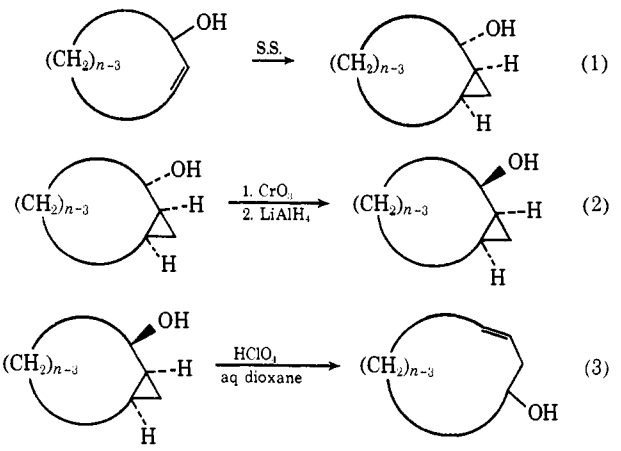




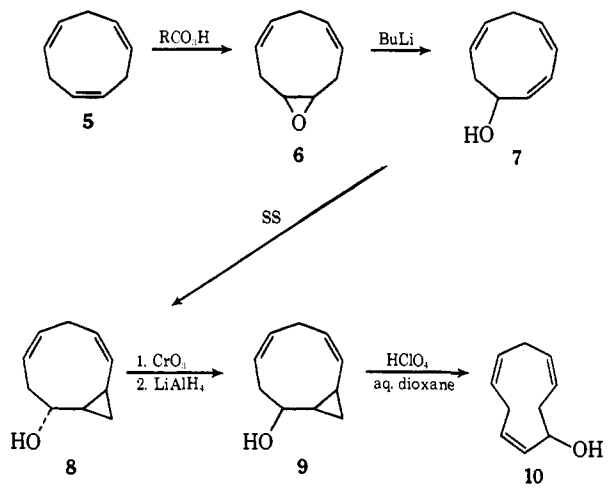
(1) (a) Acknowledgment is made to the donors of the Petroleum Research fund, administered by the American Chemical Society, for partial support of this research. (b) Research supported in part by the National Science Foundation.
(2) Address correspondence to this author at Oregon State University. NIH Postdoctoral Fellow, June 1967–Sept 1968.
(3) Deceased Nov 23, 1969.

(4) (a) M. Gasic, D. Whalen, B. Johnson, and S. Winstein, *J. Amer. Chem. Soc.*, **89**, 6382 (1967); (b) C. D. Poulter, E. C. Friedrich, and S. Winstein, *ibid.*, **91**, 6892 (1969); (c) C. D. Poulter, E. C. Friedrich, and S. Winstein, *ibid.*, **92**, 4274 (1970); (d) C. D. Poulter and S. Winstein, *ibid.*, **92**, 4284 (1970).
(5) H. E. Simmons, E. P. Blanchard, and R. D. Smith, *ibid.*, **86**, 1347 (1964), and references therein.

hols give stereospecific formation of the *anti*-methylene adduct (eq 1). Oxidation of the anti alcohol followed by hydride reduction gives highly stereospecific conversion to the syn epimer in all cases we have examined (eq 2). The homoallylic ring expansion[6] is stereospecific, *viz.*, *anti*-cyclopropyl alcohol gives only the trans double bond whereas the syn compound gives only the cis double bond (eq 3). The reaction sequence outlined in eq 1–3 makes possible the stereoselective synthesis of a variety of compounds having cis double bonds separated from other substituents by one methylene group. These are natural precursors for the corresponding compounds having cis-fused cyclopropane rings. The key intermediate in the synthetic plan is *cis,cis,cis*-2,5,8-cyclodecatrien-1-ol (**10**) which was produced by the reaction sequence shown in Scheme I.



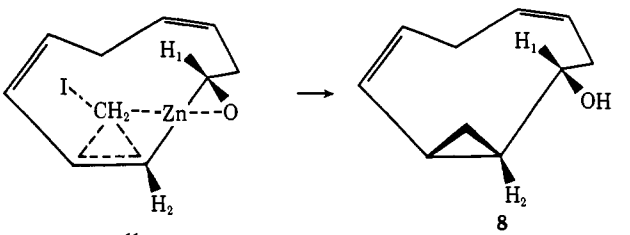
Scheme I



Treatment of *cis,cis,cis*-1,4,7-cyclononatriene[7] (**5**) with *m*-chloroperbenzoic acid gave preferential formation of the monoadduct **6**, which was treated with butyllithium[8] to give the desired alcohol, **7**.

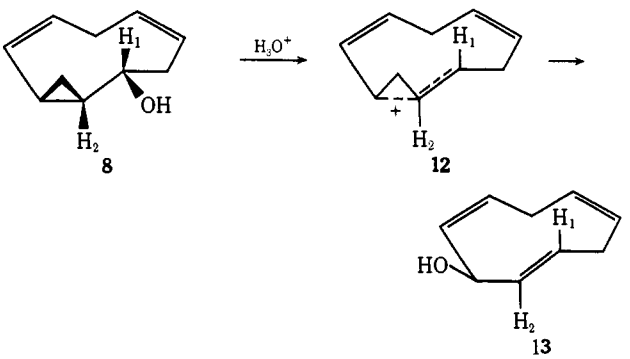
Although compound **7** has three double bonds which could react with Simmons–Smith reagent, the allylic one reacted much faster than the other two due to the rate accelerating effect of the hydroxyl group. The reaction is stereospecific giving only the anti isomer, which contrasts with the smaller ring allylic alcohols where only syn product results.[9]

This stereochemical reversal appears to be a result of the different geometry of the medium-sized ring.[4b] If one assumes that the hydroxyl group will not lie over the crowded center of the ring, the only conformations available place the protons of the 1 and 2 positions in an anti relationship, **11**, a situation not possible for the smaller rings. Thus, the directing effect is the same as

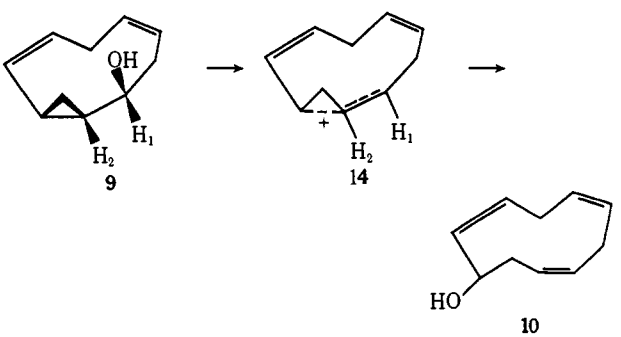


for the smaller rings but the medium-sized ring conformation changes the stereochemical outcome.

As we have reported earlier,[4] the medium-sized ring cyclopropylcarbinyl systems appear to give nonclassical ions that hold stereochemistry. Thus, solvolysis of **8** gives homoallylic ring expansion only to the trans isomer, presumably *via* the ion **12**. Since the trans



double bond stereochemistry is not desired in the present case, **8** was converted to the epimer by oxidation to the ketone followed by hydride reduction. The reduction was 98% stereoselective, probably due to steric factors. This high degree of selectivity was somewhat surprising since several possible conformations seem possible and some would predict syn while others should give anti products. This high selectivity was observed with all of the nine- and ten-membered ring α-cyclopropyl ketones in our studies. The acid-catalyzed ring



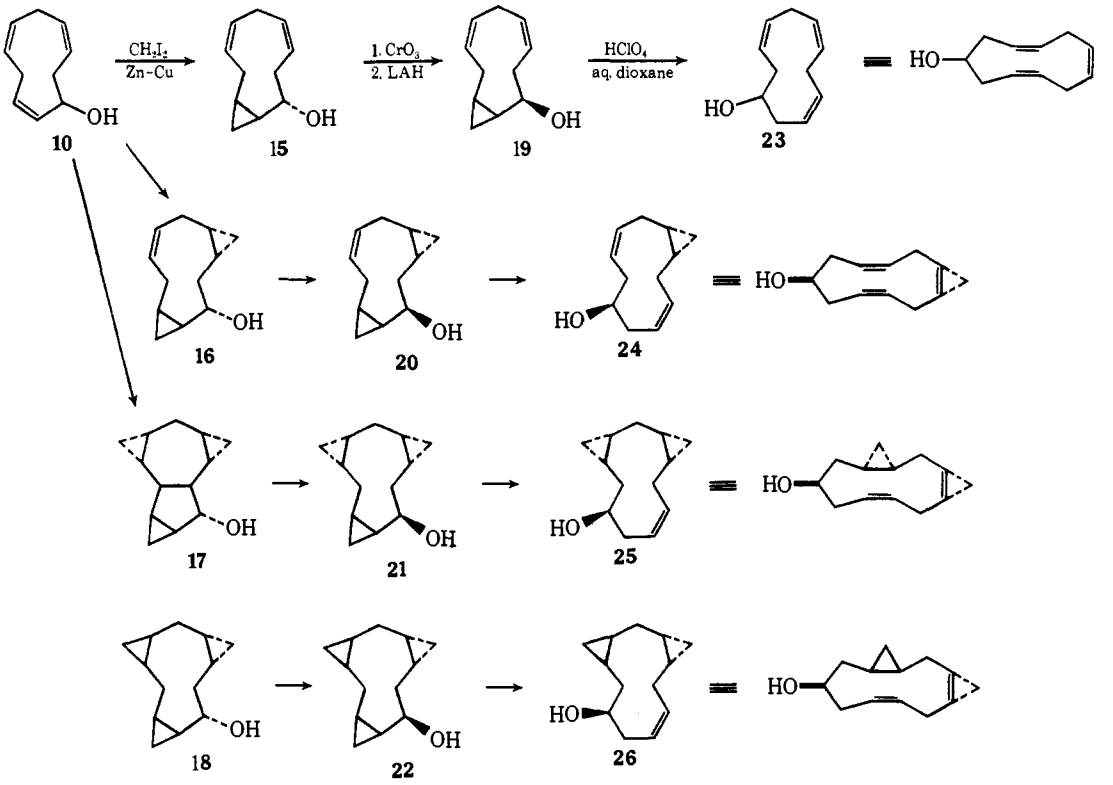
(6) (a) E. Friedrich unpublished work: (b) A. C. Cope, S. Moon, and P. E. Peterson, *J. Amer. Chem. Soc.*, **84**, 1935 (1962); (c) H. L. Goering and K. E. Rubenstein, Abstracts, 151st National Meeting of the American Chemical Society, Pittsburgh, Pa,, Mar 28-31, 1966, p 5K.

(7) P. Radlick and S. Winstein, *J. Amer. Chem. Soc.*, **85**, 344 (1963).

(8) (a) R. L. Letsinger, *et al.*, *ibid.*, **74**, 399 (1952); (b) J. K. Crandall and L. H. Chang, *J. Org. Chem.*, **32**, 435 (1967).

(9) (a) S. Winstein and J. Sonnenberg, *J. Amer. Chem. Soc.*, **83**, 3235 (1961); (b) W. G. Dauben and G. H. Berezin, *ibid.*, **85**, 468 (1963).

Scheme II



expansion gave a nearly quantitative yield of the cis double bond isomer, **10**. The stereospecific reaction appears to result from formation of the nonclassical ion **14**, in which H_1 and H_2 are cis to one another.

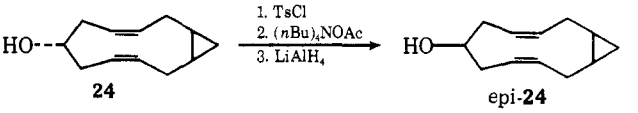
The conversion of the decatrienol **10** to precursors of the tetracyclo compounds is shown[10] in Scheme II. The Simmons–Smith reaction again gives stereospecific addition at the allylic position as the fastest reaction. Conditions can be chosen to give predominant monoadduct **15** (83:17 ratio of mono to bis) or to nearly pure bis adduct **16**. Both of these methylene additions appear to be directed by the hydroxyl group since only one isomer is formed in each case and the rates are much faster than the third methylene addition which gives a mixture of two tris adducts **17** and **18**.

The desired tetracyclo compounds could be synthesized from any of the adducts **15–18** but the best overall yield was obtained *via* **15**. In each case, the anti alcohol (**15**, **16**, **17**, or **18**) was converted to the syn epimer (**19**, **20**, **21**, or **22**) by the highly stereoselective oxidation–reduction sequence. Homoallylic ring expansion then gave the 11-membered ring with appropriately placed rings (or double bonds) and substituents, **23–26**.

The Simmons–Smith reactions on compounds **23–26** should give one or more of the six desired alcohols. The results of these and related reactions are presented in Table I. With trienol **23**, it is possible to form all six isomers and in fact all six were detected under optimum glc conditions. The predominant products **1**, epi-**1**, and **3** could be separated in fairly pure form by glc and crystallized further. The epimer of **3** could be obtained from **3** by oxidation followed by reduction and separation of the resulting epimeric mixture. There was insufficient **2** or epi-**2** to be of any use.

Since the hydroxyl could be exerting a directive effect, a more random distribution might be expected from the acetate derivative. On the contrary, the acetate gave a slightly more selective reaction than the alcohol. Although this reaction was better for making the **1** compounds (oxidation of the mixture gives 77% pure **1** ketone), the reaction gave little if any of the **2** epimers. Furthermore, none of the compounds **24–26** gave a significant amount of **2** or epi-**2**. Since part of the stereochemistry is already formed in these compounds, fewer products are possible than from **23**. For example, **24** can only give **1**, **2**, or **3** and in practice gives almost entirely **1**. Compounds **25** and **26** are stereospecific giving only **1** and **3**, respectively, even though **2** was also possible from **26** and **3** could have been formed from **25**.

One could only hope that the selectivity in the epi series would be different. Compound **24** was epimerized by conversion to the tosylate which was subsequently displaced with tetra-*n*-butylammonium acetate[11] and reduced to the alcohol, epi-**24**. The alcohol epi-**24** was then allowed to react under Simmons–Smith



conditions. Fortunately epi-**2** was a major component of the product mixture. This sequence was not a high yield one but was significant in that it was the only way that any of the **2** series were obtained. Quite possibly epi-**26** would also yield epi-**2** but insufficient material was available to test this.

It is not completely clear whether the above Simmons–Smith reactions are directed or not. The stereo-

(10) The stereochemical assignments of most of the structures in Scheme II were assigned on the basis of their conversion to the tris adducts (**1**, **2**, and **3**, and their epimers) whose stereochemistry has been assigned from nmr spectra as is herein discussed.

(11) S. Winstein, E. C. Friedrich, R. Baker, and Yang-i Lin, *Tetrahedron, Suppl.*, No. 8, 621 (1966).

Table I. Product Mixtures Resulting from Simmons–Smith or Diazomethane Reactions Leading to Tetracyclo[11.1.0.0^{3,5}.0^{7,9}]tetradecan-11-ols

Compd	Conditions	Products[a,b] 1	epi-1	2	epi-2	3	epi-3	Yield,[c] %
23-OH	SS →	42	12	1	7	33	5	58
23-OAc	SS →	55	22	?	?	15	8	55
24	SS →	98		?		2		35
	CH_2N_2, CuCl →	92		?		8		
epi-24	SS →		16		74		10	34
25	SS →	100						
26	SS →					100		
	CH_2N_2, CuCl →					100		

[a] 2 and epi-2 partially overlap with 3 and epi-1, respectively, even under our best gc conditions (50-ft DEGS capillary column, 150°). Where they are minor components, the percentages listed should be regarded as quite approximate. [b] The question marks denote no observable product, but small amounts could go undetected. [c] The unlisted yields were reactions that were too small for effective yield measurement or where reaction was not carried to completion.

specificity in some cases would argue for directed attack but the Simmons–Smith reaction with the acetate is more selective and the diazomethane reaction with the alcohols is nearly as selective. This suggests that either these reactions are also directed or that the reactions are simply controlled by steric factors.

Interconversion of the epimers is summarized in Table II. These reductions provided selective syntheses

Table II. Interconversion of Epimers

Compd	Ratio from $Al(O\text{-}i\text{-}Pr)_3$ equilibrium	Ratio from $LiAlH_4$ reduction	Ratio from $NaBH_4$, CH_3OH reduction
1	97	30	9
epi-1	3	70	91
2		35	
epi-2		65	
3	18	61	63
epi-3	82	39	37

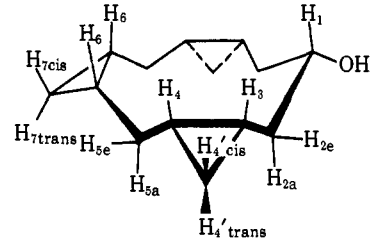
for five of the isomeric alcohols and their ketones. All were obtained in pure form except 2 which was not necessary for the stereochemical assignments since epi-2 and 2 ketone allowed assignments of the carbon skeleton.

Since none of the compounds were known, the assignment of stereochemistry was not a trivial problem. One aspect could be assigned from the method of synthesis, *viz.*, that the cyclopropane rings are cis fused. Our previous work[3] shows that each homoallylic ring expansion of a *syn*-cyclopropylcarbinyl alcohol gives a cis double bond so that the trienol **10** is all cis. Infrared bands at *ca.* 700 and none at *ca.* 960 cm^{-1} confirm the all cis assignment of **10**. The Simmons–Smith reaction is known to give stereospecific formation of the cis ring fusion[4] from cis double bonds.

The problem reduces to the determination of the configurations of the cyclopropane rings relative to one another and that of the hydroxyl group with respect to the rings. Both assignments have been made from 100-MHz spectra and decoupling experiments carried out on **1**, epi-**1**, epi-**2**, **3**, and their corresponding ketones.

In the discussion that follows, the protons have been labeled according to the number of carbon atoms between the proton considered and the hydroxyl group. This is shown in Chart I, where only the near side is shown since the numbers on the far side would be the same.

Chart I. Proton Numbering Used for the Nmr Discussion (Shown for epi-1)



The spectra for the **1** and **2** alcohols each show a clean triplet of triplets for H_1 and the A portion of AMXY patterns for H_{2e} and H_{5e}. The very large and very small vicinal coupling constants (9–11 and 1–2 Hz, respectively; see Table III) indicate that conformational

Table III. 100-MHz Spectral Data, Coupling Constants

Compd	J_{12e}	J_{12a}	J_{32e}	J_{32a}	J_{22}
1	9	1.6	3.5	?	13
epi-1	4.6	2	Small[a]	9	13
1 ketone			4.5	10	18
epi-2	7	Small[a]	Small[a]	?	12
2 ketone			4	11	17

[a] Unresolved but less than 2 Hz.

averaging does not occur. These patterns require that the **1** and **2** skeletons be symmetric about a plane passing through C_1, C_7, and the center of the C_8–C_9 bond. Alcohol **3** and its corresponding ketone do not show

Table IV. 100-MHz Nmr Spectral Data, Chemical Shifts[a] in Chloroform Solvent

Compd	H_1	H_{2e}	H_{5e}	H_{2a}	H_6, H_3, H_4, H_{5a}, $H_{4'cis}$, and $H_{7\,cis}$	$H_{4'trans}$	$H_{7\,trans}$
1	6.03	8.00	8.02	*Ca.* 9.1	8.7–9.4	10.20	10.33
epi-**1**	5.86	7.92	8.13	*Ca.* 8.6	8.5–9.4	10.38	10.23
epi-**2**	6.38	8.08	7.96	*Ca.* 8.8	8.6–9.5	10.21	9.61
3	6.20	←———		8.6–9.8	———→	10.22	9.95
1 ketone		7.24	8.10	7.94	8.6–9.7	10.33	10.57
2 ketone		7.30	7.96	7.95	8.5–9.7	10.29	9.91
3 ketone[b]		7.50	←———	7.8–8.4[c]	———→	10.40	9.95

[a] Chemical shifts are in ppm on the τ scale. [b] Chemical shifts estimated from 60 MHz spectra run in CCl_4. [c] Only three protons integrate in this region; the remaining one falls in the τ 8.4–9.7 region.

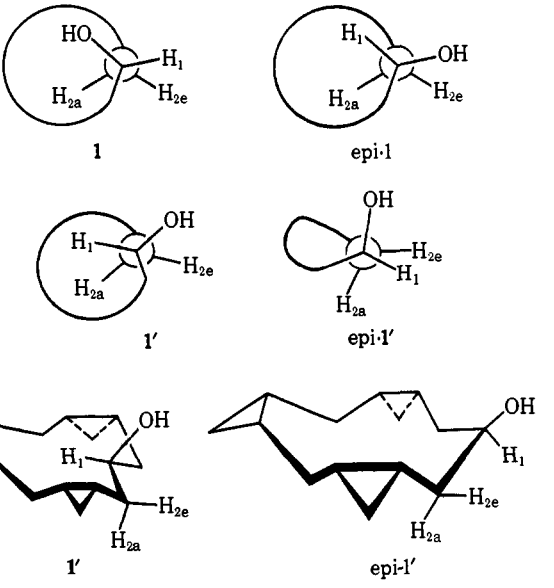
symmetrical patterns, as would be expected for the structure shown for **3** which has no element of symmetry. Thus, the carbon skeleton for the **3** series is easily assigned from symmetry but **1** and **2** are not so readily differentiated since both have the same symmetry element.

The spectral analysis of the **1** and **2** compounds is greatly facilitated by a strong preference for a single conformation, by the symmetry of the molecules and by the anisotropy of the cyclopropane rings. The latter effect causes a separation of chemical shifts which aids direct interpretation and allows decoupling experiments. A Johnson–Bovey[12] type of equation has been used in these laboratories[13] to correlate a large number of cyclopropane compounds of known stereochemistry. Protons which lie in the plane of the ring are deshielded while those over the ring are shielded. Such calculations for the **1** or **2** alcohols predicted that the chemical shifts for H_{2e} and H_{5e} should be *ca.* 100 Hz downfield from H_{2a} and H_{5a}, respectively. The tentative assignment was made on this basis and was confirmed by decoupling. In the ketones, the H_2 protons are affected by the combined anisotropies of the cyclopropane rings and the ketone group. The data of Karabatsos[14] indicates that both H_2 protons will be deshielded by the carbonyl group but that the effect on H_{2a} should be greater so that the predicted shift difference between H_{2e} and H_{2a} is 50–70 Hz for the **1** and **2** ketones.[15] The chemical-shift data are summarized in Table IV. The chemical shifts for H_1, H_{2e}, H_{2a}, and H_{5e} are well separated from the large complex pattern which contains all other protons except the high-field cyclopropane protons $H_{4'\,trans}$ and $H_{7\,trans}$. This allowed the determination of the coupling constants to these protons through decoupling experiments. These data are presented in Table III.

The carbon skeletons of the **1** and **2** compounds can be distinguished on the basis of the H_{5e} coupling constants and the chemical shift of $H_{7\,trans}$. In both the **1** and **2** compounds, $J_{4,5e}$ should be small (dihedral angle $\phi \cong 110°$). In **1**, the $J_{6,5e}$ should also be small ($\phi \cong 90°$) but for **2** predicted $J_{6,5e}$ is *ca.* 7 Hz ($\phi \cong 20°$). In addition, H_{5e} will have a geminal coupling with H_{5a} of about the same magnitude as $J_{2a,2e}$ (*i.e.*, ~13 Hz). Due to the symmetry of the molecule and the relationship of H_5, H_6, $H_{6'}$, and $H_{5'}$, coupling constants cannot be obtained directly from the spectra. However, the difference in bandwidths of the H_{5e} multiplet between the I series (~14 Hz) and the II series (~22 Hz) clearly demonstrates that the I series must have the all syn configuration. The $H_{7\,trans}$ chemical shift supports the assignment. For the **1** compounds, the $H_{4'\,trans}$ and $H_{7\,trans}$ protons have similar chemical shifts as would be expected, since they are in similar environments. In contrast, the $H_{7\,trans}$ is 40–60 Hz downfield of the $H_{4'\,trans}$ in the **2** compounds which results from its being in the equatorial plane of two cyclopropane rings (Boikeus–Brauman calculation predicts 36 Hz downfield).

The assignment of stereochemistry at C_1 is based on the vicinal coupling constants of **1** and epi-**1** which are most consistent with a crown form which has a 125° dihedral angle between H_{2e} and the axial moiety at C_1. Thus for **1**, where H_1 is equatorial, $J_{1,2e} = 9$ and $J_{1,2a} = 1.6$ Hz correlate well with dihedral angles of 5 and 125°, respectively. For epi-**1**, the couplings $J_{1,2e} = 4.6$ and $J_{1,2a} = 2$ Hz correlate with dihedral angles of 125 and 115°, respectively.

The assignment at C_1 is less certain than the previous assignments because the opposite assignment gives a reasonable correlation if it is assumed that the conformations of **1** and epi-**1** differ by a 100° rotation about C_1. Such structures are shown as **1**′ and epi-**1**′ where the dihedral angles between H_{2e} and the axial moiety at C_1 are *ca.* 180 and 80°, respectively. The coupling constants for **1**′ (9 and 1.6 Hz) then correlate with dihedral angles of *ca.* 180 and 60° while those for epi-**1**′ (4.6 and 2 Hz) would fit with angles of *ca.* 40 and 80°.



(12) C. E. Johnson and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).
(13) (a) R. S. Boikess and J. I. Brauman, unpublished results; (b) see also, D. J. Patel, M. E. H. Howden, and J. D. Roberts, *J. Amer. Chem. Soc.*, **85**, 3218 (1963).
(14) G. J. Karabatsos, G. C. Sonnichsen, N. Hsi, and D. J. Fonoglio, *ibid.*, **89**, 5067 (1967).
(15) The shifts refer to 100-MHz spectra using a crown type of conformation.

The chemical shift of H_1 argues against such an assignment. In the structures shown as **1** and epi-**1**, H_1 is in the equatorial plane of the cyclopropane rings for both epimers but is closer to these rings in epi-**1** (see Chart I). Thus, the chemical shift of H_1 for epi-**1** should be downfield of H_1 for **1**. The calculated downfield shift of 32 Hz agrees reasonably well with the observed 17-Hz downfield shift. Clearly, **1′** and epi-**1′** predict the opposite result, *viz.*, the chemical shift of H_1 for epi-**1′** was calculated to lie 42-Hz *upfield* of H_1 for **1′**.

In summary, a selective synthesis of a possible heptahomotropylium precursor has been achieved and the stereochemistry has been assigned from nmr spectra.

Experimental Section

General. Melting points were measured on a Büchi schmelzpunkbestimmungsapparat and are uncorrected. Infrared spectra were measured on a Perkin-Elmer Model 421 infrared spectrometer. Nmr spectra were measured on a Varian Associates A-60 or HA-100[16] instrument. Mass spectra were obtained on a CEC 110B instrument.[17] Elemental analyses were run by Mrs. Heather King at UCLA. Analytical gas–liquid chromatography (glc) utilized a Perkin-Elmer 800 instrument with flame ionization detectors: column A, 1/8 in. × 2 m, 2.5% KOH–2.5% Carbowax 4000 on 80–100 Chromsorb W; column **B**, 1/8 in. × 3 m, 3% diethylene glycol succinate (DEGS) on 120–140 hexamethyldisilane-treated Chromosorb W; column C, 1/8 in. × 2 m 5% Hyprose on Chromosorb W; column D, 0.01 in. × 50 ft DEGS capillary column. The flow through the 1/8-in. columns was normally 20 ml/min and temperatures of 120–169° were used. Gas chromatographic separation with collection used a Varian-Aerograph A90-P instrument: column E, 1/4 in. × 2 m, 10% DEGS on Chromosorb W; column F, 1/4 in. × 2 m, 10% Hyprose on Chromosorb W; and column G, 3/8 in. × 2 m, 10% KOH–10% Carbowax 4000 on Chromosorb W.

1,4,7-Cyclononatriene Oxide (6). A solution of 30 g of 1,4,7-cyclononatriene and 1350 ml of reagent grade methylene chloride in a 2-l. erlenmeyer flask was stirred with a magnetic stirrer and cooled to approximately 5–10° in an ice–water bath. Solid *m*-chloroperbenzoic acid (43 g, Aldrich Chemical Co.) was added over a period of 10 min. The reaction mixture was placed in the refrigerator overnight. The *m*-chloroperbenzoic acid which had precipitated from solution was collected on a Büchner funnel, and washed with methylene chloride. The filtrate was washed twice with saturated sodium bicarbonate solution and dried over anhydrous sodium sulfate. Analysis by glc on column F indicated that the ratio of 1,4,7-cyclononatriene:monoepoxide:bisepoxide was *ca.* 1:18:1. The product was purified by liquid chromatography on 180 g of Woelm neutral alumina (activity III), eluting with pentane which gave 31 g of monoepoxide **6**: mp 35–42°.

Recrystallization gave epoxide **6**: mp 50.5–51.5°; ir (CCl_4) 3008, 1639, 693 cm^{-1}; nmr (CCl_4) τ 4.0–4.8 (m, 4), 6.5–8.0 (m, 8).

Anal. Calcd for $C_9H_{12}O$: C, 79.37; H, 8.88. Found: C, 79.40; H, 9.02.

2,4,7-Cyclononatrien-1-ol (7). A solution of 40.0 g of 1,4,7-cyclononatriene epoxide and 650 ml of reagent grade ether was stirred and cooled under a nitrogen atmosphere to approximately 0° by means of a salt–ice bath. A solution of 320 ml of 1.6 *N* *n*-butyllithium in hexane (Foote Mineral Co.) was added over a period of 1 hr. The reaction solution was stirred and cooled for an additional 4.5 hr. Saturated aqueous ammonium chloride solution (200 ml) was added slowly, with cooling and stirring, over a period of approximately 1 hr. The ether solution was separated, washed with water (200 ml), and dried over anhydrous potassium carbonate. Removal of solvent yielded 45 g of a yellow oil which was distilled under reduced pressure. The first fraction (6 g) was volatile material which did not contain any alcoholic product. The later fractions, which crystallized on standing, gave 26.3 g of alcohol **7**: bp 80° (0.1 mm); mp 40–42°. The infrared spectrum was identical with the infrared spectrum of 2,4,7-cyclononatrienol prepared from acid-catalyzed rearrangement of 2,5,8-cyclononatrienol.[18]

cis,cis,exo-(anti)-**Bicyclo[7.1.0]deca-4,7-dien-2-ol (8).** A mixture of 20 g of zinc–copper couple,[19] 45 ml of ether, and 27 g of methylene iodide was refluxed 30 min with stirring under nitrogen. The reaction was cooled to room temperature and a solution of 18.2 g of trienol **7** in 72 ml of ether was added. The reaction was gently refluxed with a 40° oil bath for 2 hr as a solution of 54.9 g of methylene iodide was added dropwise. During this time the reaction turned deep purple. The reaction was monitored by glc (column A) and was 96% complete after 6 hr. Less than 1% of the bis adduct had formed at that time. The reaction was quenched at 0° by dropwise addition of 100 ml of saturated ammonium chloride solution. The ether layer was separated and washed with ammonium chloride (two 400-ml portions) and 5% sodium bicarbonate (two 100-ml portions). After the solution was dried (K_2CO_3), the product was purified by liquid chromatography on 600 g of grade II alumina, eluting with pentane and up to 30% ether–pentane. This gave 13.4 g (66.5% yield) of alcohol **8**: mp 36–38°; ir (CCl_4) 3608, 3066, 1641, 716, 656, 635 cm^{-1}; nmr (CCl_4) τ 4.1–5.0 (m, 4), 6.4–9.6 (m, 9), 9.95 (t of d, J = 6, 4 Hz, 1).

Anal. Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 79.81; H, 9.53.

The *p*-nitrobenzoate was prepared: mp 126–127°; ir (CCl_4) 1713, 1262 cm^{-1}.

Anal. Calcd for $C_{17}H_{17}NO_4$: C, 68.21; H, 5.73. Found: C, 68.61; H, 5.77.

cis,cis-**Bicyclo[7.1.0]deca-4,7-dien-2-one.** A solution of 12 g of chromium trioxide in 150 ml of water was added to a solution of 1.25 g of alcohol **8** in 150 ml of ether while cooling. The two-layer mixture was vigorously stirred. The color of the water layer gradually changed from yellow to brown and finally to green as reaction progressed and the mixture became a nearly homogeneous solution. After 3 hr the mixture was diluted with water and extracted with pentane and the pentane extracts were washed with water and dried over sodium sulfate. Solvent was evaporated and the crude oily product (1.0 g) was chromatographed on 25 g of alumina (activity II), eluting with pentane. This gave 0.72 g of bicyclo[7.1.0]deca-4,7-dien-2-one which crystallized from pentane upon refrigeration: mp 30–33°; ir (CS_2) 3010, 1695, 1630, 740, 705 cm^{-1}; nmr (CCl_4) τ 4.5 (m, 4), 6.3–9.5 (m, 8).

Anal. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 81.24; H, 8.19.

cis,cis,endo-(syn)-**Bicyclo[7.1.0]deca-4,7-dien-2-ol (9).** To a solution of 0.72 g of bicyclo[7.1.0]deca-4,7-dien-2-one in 50 ml of ether was added 0.45 g of lithium aluminum hydride. The mixture was stirred for 30 min at 0° and 30 min at room temperature. Excess hydride was decomposed with ice (external cooling) and the mixture was diluted with ether and water and filtered through Celite. The ether layer was separated, washed with water, and dried (K_2CO_3). Analysis by glc on column C showed 98% endo and 2% exo alcohol. The product was eluted from 30 g of alumina (activity II) with pentane to give 0.60 g of alcohol **9** (83% yield): ir (CS_2) 3600, 3540, 3062, 3005, 780, and 705 cm^{-1}; nmr (CCl_4) τ 4.0–4.95 (m, 4), 5.6–6.1 (m, 1), 6.2–7.8 (m, 4), 8.5–9.7 (OH and m, 4), 9.5 (t of d, J = 8, 2 Hz, 1).

Anal. Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 79.74; H, 9.52.

The *p*-nitrobenzoate was prepared in the usual way: mp 66–68°; ir (CCl_4) 1718, 1770, 1770 cm^{-1}.

Anal. Calcd for $C_{17}H_{17}NO_4$: C, 68.21; H, 5.73. Found: C, 68.27; H, 5.99.

cis,cis,cis-**2,5,8-Cyclodecatrien-1-ol (10).** A solution of 2.65 g of alcohol **9** in 100 ml of dioxane and 25 ml of 0.129 *N* perchloric acid was stirred under nitrogen at 75° while the reaction was followed by glc on column A. After 4 hr the reaction was poured into 600 ml of water and extracted into pentane (three 300-ml extractions). The pentane extracts were washed with water and saturated sodium bicarbonate and then dried (K_2CO_3). This gave 2.5 g of oil which was crystallized from 9:1 pentane–ether: mp 45–47°; ir (CS_2) 3600, 3340, 3005, 770, 745, 715, and 700 cm^{-1}; nmr (CCl_4 τ 4.2–5.1 (m, 6), 5.35 (m, 1), 6.65 (OH), 6.9–7.9 (m, 6).

Anal. Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 80.05; H, 9.33.

cis,cis,exo-(anti)-**Bicyclo[8.1.0]undeca-4,7-dien-2-ol (15).** A mixture of 5.2 g of zinc–copper couple,[19] 39 ml of ether, 6.5 g of methy-

(16) We thank Dr. Ken Servis and the Chemistry Department of the University of Southern California for allowing us to use their instrument.

(17) We thank Dr. C. Klopfenstein for measuring high-resolution mass spectra and we thank the University of Oregon Chemistry Department for the use of their mass spectrometer.

(18) Unpublished work of B. Johnson.

(19) E. LeGoff, *J. Org. Chem.*, **29**, 2048 (1964).

lene iodide, and a crystal of iodine was stirred and refluxed gently for 20 min. The reaction was cooled to room temperature and a solution of 6.2 g of trienol **10** in 39 ml of ether was added and the reaction was again gently refluxed (40° oil bath) and followed by glc on column A. After 55% of the trienol was consumed bis adduct formation was nearly as rapid as trienol consumption so the reaction was quenched and worked up as before. After the solution was dried (K_2CO_3), it was stirred with 2 g of lithium aluminum hydride for 1 hr at room temperature.[20] Excess hydride was removed by adding 10 ml of a 20% solution of potassium–sodium tartrate and the salts were removed by filtration. The solution was dried (K_2CO_3), concentrated, and chromatographed on 300 ml of SilicAR (100–200 mesh, CC-7, Mallinckrodt) eluting with pentane or up to 4% ether–pentane. This gave 3 g of pure trienol, 1 g of 50:50 trienol–monoadduct, and 2.2 g of 83% pure monoadduct. Crystallization gave 1.8 g of 97% pure monoadduct **15**. The trienol and trienol–monoadduct mixtures were then recycled. The yield for the reaction based on trienol consumed is *ca.* 65%. Crystallization gave 1.8 g of alcohol **15** (97% pure by glc, column A): mp 61–63°; ir (CS_2) 3600, 3360, 3060, 725, 715, 695 cm^{-1}; nmr (CCl_4) τ 4.0–5.0 (m, 4), 6.3–8.6 (m, 8), 8.7–10.2 (m, 4).

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.83. Found: C, 80.58; H, 9.94.

The *p*-nitrobenzoate was prepared in the usual way: mp 109–111°; ir ($CHCl_3$) 1710, 1265 cm^{-1}.

Anal. Calcd for $C_{18}H_{19}NO_4$: C, 68.99; H, 6.11. Found: C, 69.45; H, 6.37.

cis,cis,endo-(syn)-**Bicyclo[8.1.0]undeca-4,7-dien-2-ol (19).** The exo isomer **15** was oxidized and chromatographed in the same way as reported above for compound **8** which gave 70–80% yields of the ketone: ir (CS_2) 1680, 1640, 730, 700, 665 cm^{-1}; nmr (CCl_4) τ 4.2–5.0 (m, 4), 6.8–9.7 (m, 10).

Lithium aluminum hydride reduction of 0.83 g of the above ketone as described before gave the exo alcohol (>99% exo by glc on column C) which was crystallized from pentane to yield 0.6 g of alcohol **19**: mp 63–64°; ir (CS_2) 3600, 3550, 3470, 3060, 720, 690 cm^{-1}; nmr (CCl_4) τ 3.9–5.0 (m, 4), 5.9 (broad s, 1), 6.7–10.0 (m, 11).

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.83. Found: C, 80.46; H, 9.85.

The *p*-nitrobenzoate was prepared: mp 110.5–111.5°; ir (CCl_4) 1715, 1265 cm^{-1}.

Anal. Calcd for $C_{18}H_{19}NO_4$: C, 68.99; H, 6.11. Found: C, 69.11; H, 6.17.

cis,cis,cis-**3,6,9-Cycloundecatrienol (23).** A solution of 0.585 g of alcohol **19**, 24 ml of dioxane, and 6 ml of 0.03 *M* perchloric acid was stirred under nitrogen for 100 min at 75°. The reaction was worked up as described previously which gave 0.580 g of trienol **23** (single peak on glc) which was crystallized from pentane: mp 65–67°; ir (CS_2) 3600, 3400, 3005, 720, 710 cm^{-1}; nmr (CCl_4) τ 4.3–5.2 (m, 6), 6.0–6.5 (OH and m, 2), 7.1–7.5 (m, 4), 7.6–8.0 (broad triplet, $J \cong 6$ Hz, 4).

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.83. Found: C, 80.44; H, 9.71.

The *p*-toluenesulfonate was made in the usual way, mp 51.5–53°.

Anal. Calcd for $C_{18}H_{22}O_3S$: C, 67.91; H, 6.97. Found: C, 68.03; H, 7.02.

cis,exo,exo-**Tricyclo[9.1.0.0^{4,5}]dodeca-7-en-2-ol (16).** A mixture of 4.91 g of zinc–copper,[19] 2.8 g of methylene iodide, 10 ml of ether, and a crystal of iodine was refluxed under nitrogen for 20 min (oil bath at 50°). After cooling to room temperature (*ca.* 10 min), 3.45 g of cyclodecatrienol in 10 ml of ether was added and the reaction mixture was brought to reflux. After 20 min, 10.2 g of methylene iodide and 5 ml of ether were added. The reaction mixture turned purple after 20 min, at which time a Dean–Stark head was used to distill off 10 ml of solvent which was replaced with dry ether.[21] This was repeated twice and then reflux was continued as the reaction was monitored by glc on column A. Three hours from the time of alcohol addition, the reaction mixture was cooled, diluted with ether, and quenched with saturated ammonium chloride (3% mono, 91% bis, 6% tris). The reaction mixture was decanted from the solid precipitate and the ether layer was washed with saturated ammonium chloride, saturated sodium bicarbonate, and saturated sodium chloride solution. After drying over potassium carbonate, the excess methylene iodide was removed by stirring the ether solution with 2 g of LAH. Excess LAH was decomposed by dropwise addition under nitrogen of 25 ml of a 20% solution of sodium–potassium tartrate. After drying over potassium carbonate, the crude product was chromatographed on 100 g of SilicAR (CC-7, Mallinckrodt) which gave 4 g of oil. Crystallization from 40 ml of pentane at freezer temperature gave 2.6 g (45% yield) of crystals. The glc indicated about 12% of an early retention time material but this appears to be due to elimination on the glc column. Disregarding the 12% peak, the bis adduct was 98% pure on glc: ir (CS_2) 3600, 3460, 3060, 685 cm^{-1}; nmr (CCl_4) τ 4.2–5.0 (m, 2), 6.5–7.2 (m, 1), 7.2–8.3 (m, 7), 8.3–10.2 (m, 8).

cis,exo,endo-**Tricyclo[9.1.0.0^{4,5}]dodec-7-en-2-ol (20).** Alcohol **16** was converted to its epimer using the same conditions reported above for compound **8**. An overall yield of 73% was obtained for oxidation to the ketone (mp 37–40°; ir (CS_2) 3060, 1680, 695 cm^{-1}) followed by lithium aluminum hydride reduction, chromatography on SilicAR, and crystallization from pentane: mp 83–84°; ir (CS_2) 3600, 3400, 3060, 3000, 675 cm^{-1}; nmr (CS_2) τ 4.2–4.5 (m, 2), 5.3–5.7 (m, 1), 6.5–6.7 (m, 1), 7.3–7.8 (m, 3), 7.8–9.4 (m, 9), 9.4–9.7 (m, 1), 9.9–10.2 (m, 1).

Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.78; H, 10.00.

cis,cis,exo-**Bicyclo[9.1.0]dodeca-3,8-dien-6-ol (24).** A solution of 1.9 g of **20** in 160 ml of dioxane and 40 ml of 0.13 *N* perchloric acid solution was stirred and heated at 75° under nitrogen. The reaction was followed by glc on column A. After 1 hr, the reaction mixture contained only a small amount of starting alcohol, 85% of the desired product, and 15% of a by-product with similar retention time to starting alcohol. The reaction was quenched and worked up as above. Column chromatography on 35 g of SilicAR gave 1.1 g of alcohol **24**: mp 62–66°; ir (CS_2, 3600, 3320, 3060, 707, 690 cm^{-1}; nmr (CCl_4) τ 4.4–5.1 (m, 4), 6.3 (m, 1), 6.87 (OH), 7.3–8.5 (m, 8), 9.0–10.2 (m, 4); calcd *m/e* for $C_{13}H_{18}O$, 178.136; found *m/e* 178.136.

Tetracyclo[10.1.0.0^{3,5}.0^{7,9}]tridecan-11-ols, 17 and 18. A mixture of 4.32 g of zinc–copper couple,[19] 3.0 g of methylene iodide, and 8 ml of ether was stirred and allowed to reflux under nitrogen for 30 min. The mixture was cooled to room temperature and a solution of 1.0 g of trienol **10** in 12 ml of ether was added. The reaction was stirred alternately at room temperature or in a 40° oil bath, just to maintain gentle reflux, and 11.1 g of methylene iodide was added in portions over 1 hr. After 6 hr at 45°, the reaction was worked up as described above. This gave two tris adducts (**17** and **18** in a ratio of 1.3:1) and a small amount of bis adduct (*ca.* 5%). The tris adducts were separated by glc on column G yielding 303 mg of **17** and 155 mg of **18**. Compound **17** possessed spectral properties as follows: ir (CS_2) 3600, 3055 cm^{-1}; nmr (CCl_4) τ 6.7–7.6 (m, 2), 7.6–9.9 (m, 15), 9.9–10.8 (m, 3).

Anal. Calcd for $C_{13}H_{20}O$: C, 81.20; H, 10.48. Found: C, 80.79; H, 10.50.

For **18** the following characteristics were observed: mp 57–61°; ir (CS_2) 3600, 3060 cm^{-1}; nmr (CCl_4) τ 6.4 (m, 1), 7.2–10.0 (m, 17), 10.0–10.4 (m, 2).

endo,exo,exo-**Tetracyclo[10.1.0.0^{3,5}.0^{7,9}]tridecan-10-ol (21).** A 275-mg portion of **17** was oxidized with chromium trioxide as described above to the ketone: ir (CS_2) 3060, 1677 cm^{-1}; nmr (CCl_4) τ 7.1 (d of d, $J \cong 5$ and 17 Hz, 1), 7.4–10.1 (m, 15), 10.1–10.6 (m, 2). Lithium aluminum hydride reduction gave 199 mg of alcohol **21** (contaminated with 4% of **17**) which was then crystallized: mp 73–76.5°; ir (CS_2) 3605, 3585 cm^{-1}; nmr (CCl_4) τ 5.52 (broad d, $J \cong 8$ Hz, 1), 6.28 (OH), 7.3–9.9 (m 16) 10.0–10.6 (m 2).

endo,exo-**Tricyclo[10.1.0.0^{3,5}]tridec-9-en-7-ol (25).** Compound **21** (187 mg) was subjected to acid-catalyzed ring expansion as described above which gave 129 mg of **25**: mp 77–81°; ir (CS_2) 3600, 3055, 680 cm^{-1}; nmr (CCl_4) τ 4.5–5.0 (m, 2), 6.0–6.5 (OH and m, 2), 7.2–9.9 (m, 14), 10.0–10.5 (m, 2).

Anal. Calcd for $C_{13}H_{20}O$: C, 81.20; H, 10.48. Found: C, 81.10; H, 10.22.

exo,exo,endo-**Tetracyclo[10.1.0.0^{3,5}.0^{7,9}]tridecan-10-ol (22).** Alcohol **18** was oxidized to the ketone with chromium trioxide and chromatographed as above (75% yield): mp 30–33°; ir (CS_2) 3060, 1678 cm^{-1}; nmr (CCl_4) τ 7.2 (d of d, J = 4 and 16 Hz, 1), 7.5–9.7 (m, 15), 9.7–10.3 (m, 2).

Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.54. Found: C, 81.79; H, 9.52.

Lithium aluminum hydride reduction gave a 97% yield of **22**: mp 93–95°; ir (CS_2) 3600, 3060 cm^{-1}; nmr (CCl_4) τ 5.8 (m, 1), 7.1–10.2 (m, 19).

(20) This step was intended to remove excess methylene iodide. On larger reactions, an alternative is to stir with methanolic sodium methoxide for 2 days.

(21) R. Ginsig and A. D. Cross, *J. Amer. Chem. Soc.*, **87**, 4629 (1965).

Anal. Calcd for $C_{13}H_{20}O$: C, 81.20; H, 10.48. Found: C, 81.34; H, 10.64.

exo,exo-**Tricyclo[10.1.0.0^{3,5}]tridec-9-en-7-ol (26).** Alcohol **22** was ring expanded as above (quantitative) to give **26**: mp 84–85.5°; ir (CS_2) 3600, 3060, 682 cm^{-1}; nmr (CCl_4) τ 4.2–5.2 (m, 2), 6.3 (m, 1), 6.6 (OH and m, 2), 7.1–10.2 (m, 14), 10.4 (m, 1).

Anal. Calcd for $C_{13}H_{20}O$: C, 81.20; H, 10.48. Found: C, 81.05; H, 10.64.

Tetracyclo[11.1.0.0^{3,5}.0^{7,9}]tetradecan-11-ols (1, epi-1, 2, epi-2, 3, epi-3). Method A (*via* 3,6,9-Cycloundecatrienol). A mixture of 2.1 g of zinc–copper couple,[19] 5 ml of ether, 2.0 g of methylene iodide, and a crystal of iodine was gently refluxed with stirring under nitrogen for 30 min and then cooled to room temperature. A solution of 0.45 g of trienol **23** in 5 ml of ether was added followed by dropwise addition of 5.0 g of methylene iodide in 5 ml of ether over 1 hr while heating with a 40° oil bath. Reaction progress was followed by glc on column A. After 5 hr, the reaction mixture was quenched and washed with saturated ammonium chloride, dried over potassium carbonate, and chromatographed on 25 g of activity II alumina (pentane and up to 50% ether–pentane eluent). This gave 0.33 g (58% yield) of tetracyclic alcohols which were further purified by glc on column F and crystallization.

Method B (*via* 3,6,9-Cycloundecatrienyl Acetate). The acetate was prepared by heating 1.0 g of **10**, 4.0 g of acetic anhydride, and 50 ml of pyridine for 1 hr and working up in the usual way. Chromatography on SilicAR gave 0.95 g of acetate (75% yield).

A mixture of 10 g of zinc–copper couple,[19] 10 g of methylene iodide, and 30 ml of ether was stirred and refluxed under nitrogen for 20 min. To this mixture was added a solution of 0.95 g of acetate in 10 ml of ether followed by 10 g of methylene iodide. The reaction was stirred and heated with a 50° oil bath for 7 hr and worked up as above. SilicAR chromatography gave 1.5 g of tetracyclic acetates which were reduced with lithium aluminum hydride. This gave 0.68 g (55% yield from cycloundecatrienol) of tetracyclic alcohols.

Method C (*via* 24). The Simmons–Smith reaction was run essentially as shown above for method A.

Method D (*via* epi-24). Compound **24** was epimerized by conversion to the tosylate followed by displacement with tetra *n*-butylammonium acetate.[10] The displacement was carried out by heating a solution of 6.97 g of tosylate, 5.8 g of tetra-*n*-butylammonium acetate, and 20 ml of dry acetone in a sealed ampoule for 70 hr at 65°. The mixture was extracted into pentane, washed with water and 5% bicarbonate, and dried ($MgSO_4$). The acetate was chromatographed on alumina (activity III), reduced with lithium aluminum hydride, and chromatographed again on activity III alumina. This gave 0.170 g of the epi-**24** (30% yield for the entire epimerization) contaminated with an unknown 10% impurity: ir (CS_2) 3600, 3320, 3060, 712 cm^{-1}; nmr (CCl_4) τ 4.3–5.0 (m, 4), 6.0–6.3 (m, 1), 6.7 (OH), 7.1–8.2 (m, 8), 9.0–10.0 (m, 4).

Several Simmons–Smith variations were tried because yields were quite low. The best was a variation of the Cross–Ginsig procedure.[21] A mixture of 0.25 g of zinc–copper couple,[22] 2 ml of dry ether, and 0.6 ml of methylene iodide was stirred and refluxed for 15 min. A solution of 0.110 g of alcohol epi-**24** (90% pure by glc) in 0.5 ml of ether was added over a 1-hr period. One-half of the solvent was distilled from the reaction mixture and replaced with dry ether. The reaction was followed by glc on column A and quenched with ammonium chloride after 5.5 hr. The work-up was as described above. Chromatography gave 0.043 g (34% yield) of tetracyclic alcohols.

Method E (*via* 25 or 26). A mixture of 127 mg of zinc–copper[19] and 90 mg of methylene iodide in 0.7 ml of ether was stirred and refluxed under nitrogen for 30 min. A solution of 105 mg of compound **25** (or **26**) in 0.7 ml of ether was added, followed by 90 mg of methylene iodide. The mixture was stirred and heated with 45° oil bath and, during the course of the next 45 min, 263 mg of methylene iodide was added. After an additional 6.5 hr the reaction was quenched and worked up as above.

Method F (Diazomethane). Conditions used were those reported by Doering and Roth.[23]

All of the above methods gave mixtures of tetracyclic alcohols (see Table I) which were separated by column chromatography, glc, and crystallization, yielding pure samples of **1**, epi-**2**, epi-**2**, and **3**.

The ketones were prepared by oxidation with chromium trioxide as described above for oxidation of compound **8** (*ca.* 70% yield). The nmr spectra have been presented in a previous section. The analyses are given below and other relevant data are shown in Table V.

Table V. Physical and Spectral Data for the Tetracyclo[11.1.0.0^{3,5}.0^{7,9}]tetradecanyl Alcohols and Ketones

Compd	Mp, °C	*R*. value[a]	Retention[b] time, min	Infrared (CS_2), cm^{-1}
1	124–125	0.25	27.5	3610, 3590, 3400, 3055
epi-**1**	91–92	0.31	30.5	3680, 3600, 3450, 3050
2	?	?	33.5	
epi-**2**	97–101	0.27	31.5	3600, 3350, 3050
3	109–112	0.24	34.3	3620, 3360, 3060
epi-**3**	113–116	?	36.4	3600, 3460, 3050
1 ketone	132.5–134	0.39	20.9	3060, 1715
2 ketone	117–121	0.61	19.7	3060, 1713
3 ketone	69–71	0.46	23.8	3055, 1700

[a] 5 × 20 SilicAR (Mallinckrodt) plates eluted with 30% ether–petroleum ether. [b] Column D at 150°.

Anal. Calcd for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found for **1**: C, 81.33; H, 10.54. Found for epi-**1**: C, 81.21; H, 10.90. Found for **3**: C, 81.91; H, 10.92.

Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found for **1** ketone: C, 82.56; H, 9.73. Found for **3** ketone: C, 82.39; H, 9.57.

Calcd *m/e* for $C_{17}H_{30}OSi$: 278.203. Found *m/e* for the trimethylsilyl derivative of epi-**2**: 278.205.

Reductions of the Tetracyclo[13.1.0.0^{3,5}.0^{7,9}]tetradecanones. Method A ($LiAlH_4$). A 5-mg portion of lithium aluminum hydride was added to a solution of 5 mg of ketone in 1 ml of ether at 0 to −5° and stirred for 5 hr. The reaction was quenched with 1 ml of 20% sodium–potassium tartrate solution and extracted into ether and dried (K_2CO_3).

Method B ($NaBH_4$). To a solution of 5.0 mg of ketone in 1 ml of methanol was added 5 mg of sodium borohydride at −40°. The mixture was stirred for 9 hr and then quenched with 1 ml of 20% sodium hydroxide and extracted in 10 ml of ether. The ether layer was washed with saturated sodium chloride solution and dried over magnesium sulfate.

Method C (Aluminum Isopropoxide). A mixture of 3.0 mg of ketone, 100 mg of aluminum isopropoxide, and 2 ml of dry isopropyl alcohol was stirred under nitrogen at 100° for 48 hr. The mixture was quenched with 2 ml of 20% potassium hydroxide solution and extracted into ether. The ether layer was treated as above.

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