The Stereochemistry of the Pentadienyl–Cyclopentenyl Cation Rearrangement

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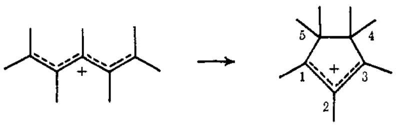
Abstract: The rearrangement of dienylic cations into cyclopentenyl cations is stereospecific and follows the predictions of Woodward and Hoffmann. The stereospecificity is not 100% and it is believed that some isomerization occurs at the dienylic ion stage. An attempt was made to prepare the carbonium ions under as wide a spectrum of conditions as possible in order to be quite certain about the significance of the results.

Many examples are now known[1–5] in which a substituted pentadienyl cation undergoes a cyclization reaction to yield a cyclopentenyl cation.



I II

This reaction has been treated theoretically by Woodward and Hoffmann and can be described as an electrocyclic transformation.[6] A consideration of the symmetry of the highest occupied molecular orbital leads to the prediction that ring closure should occur in a conrotatory manner for a thermal process.

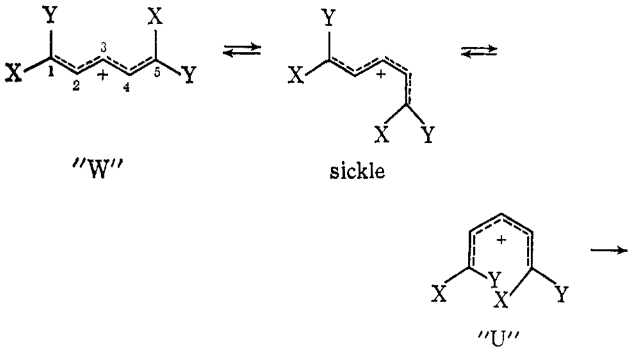
In the examples studied to date, a further rearrangement of the cyclopentenyl cation has destroyed any stereochemistry initially present at C_4 and C_5.

The present study was formally undertaken in order to test the predicted stereospecificity of this reaction but the absence or presence of a stereospecific cyclization process would actually yield a good deal of information on the structure of the ions, a point to be discussed later.

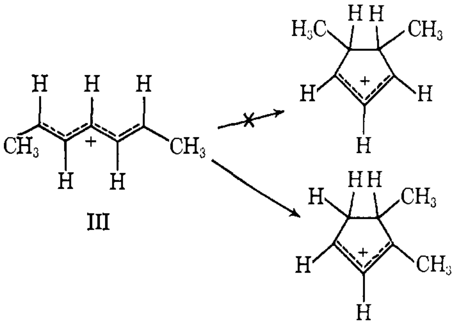
The requirements for a successful study are as follows.

1. The ends of the dienylic ion must be substituted with two different groups. In the present work, these were chosen as methyl and hydrogen (X = H, Y = CH_3).

2. The most stable form for a dienylic cation is probably the "W" or all-*trans* form.[7] In order for cyclization to occur one must get "conformational" changes ending with the "U" form. The rotations for these processes occur about the 2–3 and 3–4 bonds, predicted from HMO theory to have a π-bond order of 0.577. Rotations about the bonds 1–2 or 4–5, which destroy any stereochemistry impressed on the system, have a π-bond order of 0.788, not greatly different. Alternately, a σ-bonded counterion may be involved in these interconversions.

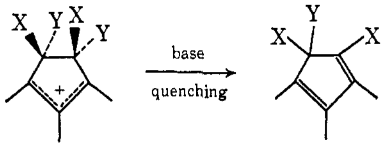


3. The cyclopentenyl ion II (*cis* or *trans* at C_4 and C_5), must be stable to uncontrollable interconversions between the *cis* and *trans* isomers and to isomerizations destroying the stereochemical centers. Previous examples of this reaction have failed at this stage. For example, the cyclization of III produces as the first *observable* product, the rearranged ion IV, with no stereochemical possibilities.[3]



III IV

4. It must be possible to detect the *cis* and *trans* cyclic ions by nmr spectroscopy since the usual quenching experiments, which would be the only practical alternative method of analysis, are expected to yield mainly a cyclopentadiene, destroying the stereochemistry present in the ions. In theory, other quenching methods designed to preserve the stereochemistry are however possible.



cis (or *trans*)
Y = H

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[1] N. C. Deno and C. U. Pittman, Jr., *J. Am. Chem. Soc.*, **86**, 1871 (1964).

[2] T. S. Sorensen, *Can. J. Chem.*, 42, 2768 (1964).

[3] T. S. Sorensen, *ibid.*, 43, 2744 (1965).

[4] N. C. Deno, C. U. Pittman, Jr., and J. O. Turner, *J. Am. Chem. Soc.*, **87**, 2153 (1965).

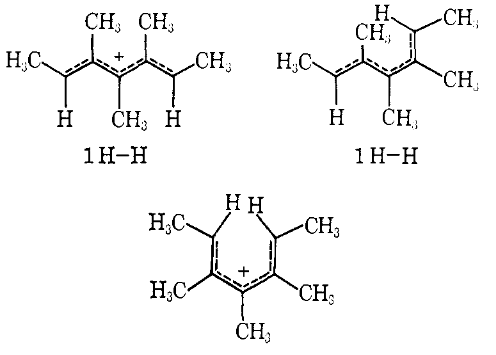
[5] T. S. Sorensen, *ibid.*, **89**, 3782, 3794 (1967).

[6] R. B. Woodward and R. Hoffmann, *ibid.*, **87**, 395 (1965).

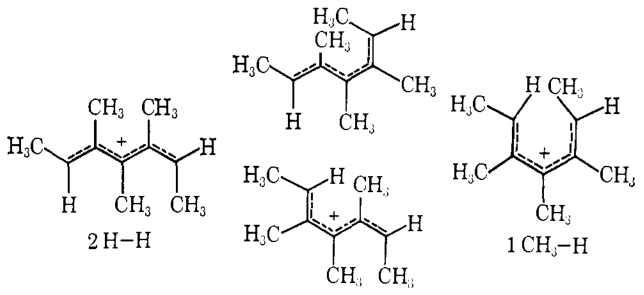
[7] T. S. Sorensen in "Carbonium Ions," Vol. II, G. Olah and P. R. Schleyer, Ed., John Wiley & Sons, Inc., New York, N. Y., 1969, Chapter 19.

Several studies relating to the one at hand have been published. Woodward[8] has shown that the Nazarov cyclization, which most probably involves a hydroxyldienylic cation intermediate, can take place in a stereospecific manner. Winstein and Childs[9] have demonstrated that benzenonium ions (dienylic cations) undergo a photochemical ring closure. The stereochemistry is of course restricted to a *cis* junction but the facile nature of the process and the difficulty in the reverse step are exactly as predicted. The related pentadienyl anion has been observed to undergo a stereospecific ring closure to give a cyclopentenyl anion.[10]

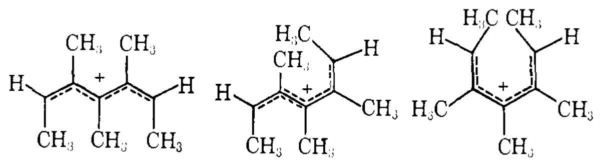
The system chosen for the present study was the 3,4,5-trimethylheptadienyl cation (VA, B, C), which can theoretically exist in three geometric modifications, each of these in turn having three or four possible "conformations" (W, sickle, and U).


1 H-H 1 H-H 1 H-H

VA

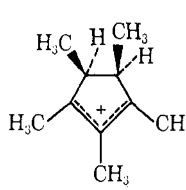

2 H-H 2 H-H 1 CH_3-H

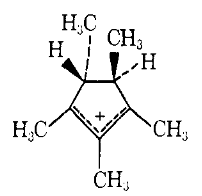
VB


3 H-H 1 H-H + 1 CH_3-H 1 CH_3-CH_3

VC

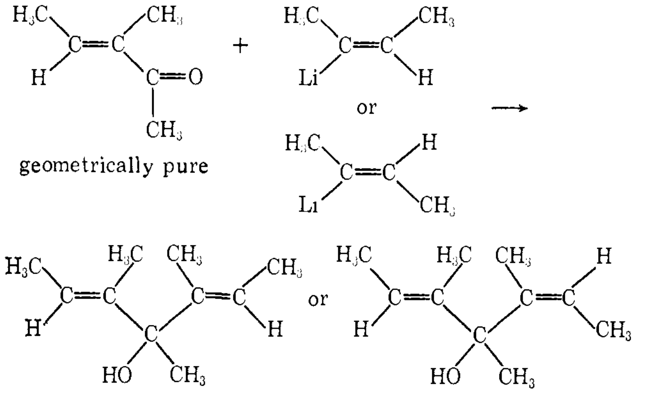
On cyclization, one would predict the formation of *cis*- or *trans*-1,2,3,4,5-pentamethylcyclopentenyl cation (VIA or B). From previous work in this laboratory,[5] one can be reasonably certain that the base-catalyzed interconversions of these two ions will be very slow if one chooses the proper acid systems. The possibility of hydride shifts occurring after the initial cyclization cannot be ruled out.[5] This system, however, meets criteria 1 and probably 4 as discussed above. Criteria 2 and 3 can be tested only by experiment.


VIA

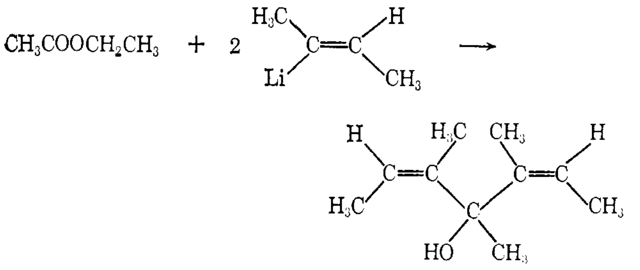

VIB

Results

Dienylic ions have previously been prepared from either a triene or a dienol. One cannot fix the complete stereochemistry using trienes or conjugated dienols and the only feasible precursers for the preparation of V would be the unconjugated dienols VIIA, B, and C, which were prepared as follows. The *cis*- and *trans*-2-butenyllithium system has been carefully studied by several investigators[11] and it has been shown that the reaction is nearly stereospecific in going from the vinyl bromide to the lithium derivative. Reported[11] examples of isomerization in this reaction seem to be in part the result of isomerization of the vinyl bromides. The *cis*-2-bromobut-2-ene is readily isomerized to the *trans* isomer, but by completing the preparation of the bromobutene and the lithium compound in a short period of time and not attempting to distill the crude *cis*-bromobutene, one can obtain reasonably good geometric purity in the alcohols. The bromobutenes are readily analyzed by glc so that one can determine the geometric purity of the starting material immediately prior to reaction. It proved feasible to analyze the purity of the three alcohols by nmr spectroscopy (see Experimental Section), and fortunately each one can be separated from small amounts of the isomeric alcohols by careful fractional distillation under reduced pressure.



VIIA VIIB


VIIC

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(8) R. B. Woodward in "Aromaticity," The Chemical Society, London, 1968.

(9) R. F. Childs and S. Winstein, *J. Am. Chem. Soc.*, **90**, 7146 (1968).

(10) R. B. Bates and D. A. McCombs, *Tetrahedron Lett.*, **12**, 977 (1969).

(11) (a) A. S. Dreiding and R. J. Pratt, *J. Am. Chem. Soc.*, **76**, 1902 (1954); (b) F. G. Bordwell and P. Landis, *ibid.*, **79**, 1593 (1957).

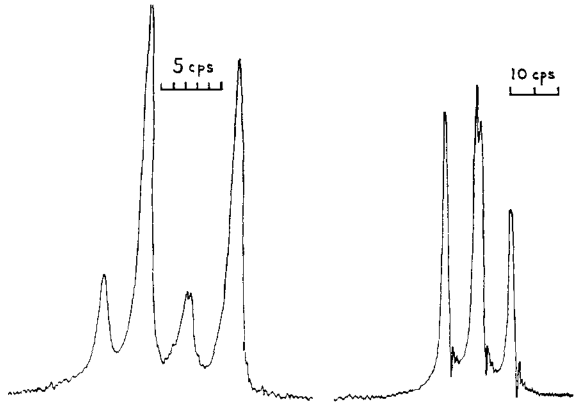

Figure 1. Nmr spectrum in fluorosulfonic acid solvent of two separate mixtures of cations VIA and VIB: left, 60 mc spectrum at 100-cps sweep width; right, 100-mc spectrum at 250-cps sweep width.

Compounds VIIA and B were obtained in >99% purity (no other compound apparent), while VIIC could be obtained in 97–98% purity (the impurity is VIIB). The structure of the alcohols follows from the method of synthesis and is in agreement with the nmr spectra. For example, the 2 (or 6) hydrogen of the *cis*- and *trans*-butenyl groups (a quartet of quartets) are well separated (0.23 ppm), the two symmetric isomers showing only one set of double intensity while the unsymmetrical isomer shows both sets in approximately the same position as found in the symmetrical isomers.

Synthesis of the Ions. It proved not possible to observe the dienylic ions (VA, B, C) as hoped. At −80°, there is no trace of an open-chain dienylic ion (measured within 5 min of preparation). Even during the preparation there is no transient color such as might be associated with this ion (expected λ_{max} *ca.* 380 mμ).[2] Dienylic ions vary enormously in their rates of cyclization and the above result was not entirely unexpected.[2] The only carbonium ion observed was VI. However, it was found that the alcohols VIIA, B, and C gave *different* carbonium ion nmr spectra and that these differences could be interpreted as varying ratios of the *cis* and *trans* isomers, VIA and B. Figure 1 shows the pertinent region of the spectrum (60 and 100 mc) showing the peaks due to the two ions. This region should be the A_3 part of two different $A_3XX'A_3'$ systems (assuming no coupling with protons on C_1, C_2, or C_3). Published spectra of this type are complex[12] but in the ions VIA and B the A system resembles a simple A_3X case, with some line width differences apparent, particularily at 60 mc, between the *cis* and *trans* isomers.

The ratio of the two isomers formed proved to be quite sensitive to the conditions used to prepare the ions and a complete study was undertaken, employing eight different acid media, preparation at two or three different temperatures, and a number of methods of introducing the alcohols into the acid. These are outlined in Table I. All of the ratios reported were measured under controlled conditions where it can be shown that the isomerization of the *cis* isomer to the *trans*, or *vice versa*, is not occurring. The *cis*/*trans* ratio was obtained in all cases from both 60- and 100-mc spectra, which are different in appearance and in the actual analysis used (Figure 1). All results at each set of conditions were done at least twice and in some cases four to eight times. The actual reproducibility varied considerably and it may be that one should report a range rather than an average.

Table I. Initial Ratios of VIA and VIB Obtained

		Temp[b] of addition, °C	% *trans*-VIB		% *cis*-VIA	
Acid[a]	Alcohol		Av	Best[c]	Av	Best[c]
95% H_2SO_4	VIIA	−5	85		15	
	VIIB	−5	12	7	88	93
	VIIC	−5	82		18	
99% H_2SO_4	VIIA	−5	83		17	
	VIIB	−5	9	6	91	94
	VIIC	−5	79	83	21	17
20% fuming H_2SO_4	VIIA	0	74		26	
		−12	83		17	
	VIIB	0	23		77	
		−12	23	16	77	84
	VIIC	0	68		32	
		−12	82		18	
$ClSO_3H$	VIIA	0	74		26	
		−80	88	92	12	8
	VIIB	0	50		50	
		−80	34		66	
	VIIC	40	50		50	
		0	52		48	
		−80	72		28	
FSO_3H	VIIA	0	70		30	
		−80	88	94	12	6
	VIIB	0	53		47	
		−80	22		78	
	VIIC	0	64		36	
		−80	78		22	
CF_3SO_3H	VIIA	0	69		31	
		−40	73		27	
	VIIB	85	75		25	
		0	67		33	
		−40	53		47	
	VIIC	75	75		25	
		21	72		28	
		−40	62		38	
20% $S_2Cl_2O_5$ in $ClSO_3H$	VIIA	0	75		25	
		−80	80	83	20	17
	VIIB	0	43		57	
		−80	21	18	79	82
	VIIC	0	59		41	
		−80	68		32	
1:1 FSO_3H–SbF_5	VIIA	0	70		30	
		−80	73	76	27	24
	VIIB	0	52		48	
		−80	40	37	60	63
	VIIC	0	61		39	
		−80	71		29	

[a] *Ca.* 10% w/v solutions. [b] Cooling bath temperature—solutions occasionally froze and had to be warmed slightly from time to time. [c] Included where there is a significant difference between the best and the average.

The position of the nmr peaks in the two ions are reported in Table II.

Table II. Nmr Spectral Data for the Carbonium Ions[a]

Ion	Peaks			
	1 and 3 CH_3[b]	$2CH_3$	4 and 5 CH_3[c]	4 and 5 H
VIA	7.225, 7.24, 7.265, 7.28	7.90	8.645, 8.72, $J = 7.5$ cps	6.60[d]
VIB	7.23, 7.25, 7.26, 7.275	7.90	8.58, 8.645, $J = 7.1$ cps	7.05[e]

[a] 10 w/v in $ClSO_3H$ run at 100 mc. Values are relative to external TMS = 10 ppm. [b] Coupling is probably with C_4 and C_5 protons. [c] In some spectra (FSO_3H and CF_3SO_3H solvents) it is possible to resolve partially the center peak. [d] Very broad, *ca.* 0.18 ppm at half-height, no resolution apparent. [e] *Ca.* 0.20 ppm at half-height.

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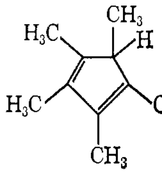
(12) (a) A. A. Bothner-By and C. Naar-Colin, *J. Am. Chem. Soc.*, 84, 743 (1962); (b) F. A. L. Anet, *ibid.*, 84, 747 (1962).

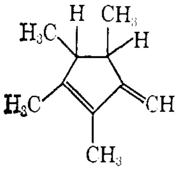
Cryoscopic Measurements. An *i* factor of 4.1–4.2 was found in the preparation of the ion VI, using the alcohols and sulfuric acid solution. This value is in good agreement with that predicted for the equation $ROH + 2H_2SO_4 \rightarrow H_3O^+ + 2HSO_4^- + R^+$. There is no question therefore, about the nature of the species observed in the nmr spectra.

Ultraviolet Spectra. The ultraviolet spectra of VIA and B were obtained in chlorosulfonic acid solution, VIA had λ_{max} equal to 297 mμ (ϵ_{max} *ca.* 8200); VIB had λ_{max} 299 mμ (ϵ_{max} *ca.* 11,000). These values are in good agreement with the spectral results from other allylic cations[5] but are obviously too close together for any use as an analytical tool.

Equilibration of the Ions. In all of the solvents reported in Table I, with the exception of 95 and 99% sulfuric acids, there is no noticeable change in the initial ratio of the two ions VIA and B, after 10 days at 25°. With sulfuric acids, it is possible to observe the equilibration reaction taking place and to measure both the kinetics of this reaction and the dependence of the rate on the per cent sulfuric acid used as the solvent.[13] The equilibrium constant for this system in 95 or 99% sulfuric acid is 3.9 ± 0.3 favoring the *trans* isomer. These ions can also be prepared in lower per cent sulfuric acid solutions but the isomerization reaction is too rapid for one to obtain an accurate initial ratio.

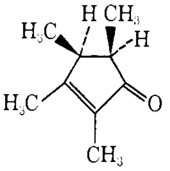
Recovery Experiments. The normal quenching procedures employed in the past[2] produced a 90% yield of $C_{10}H_{16}$ hydrocarbons, consisting of 1,2,3,4,5-pentamethylcyclopentadiene (VIII), 92%, and an exocyclic methylene compound (IX), 8%. The exocyclic diene may have either the *cis* or *trans* geometry, or more likely is a mixture of both. Since the ion preparation usually does not give better than a 90:10 mixture of isomers and since the ratio of VIII/IX might vary individually in the case of each ion, the 8% yield of IX would not necessarily reflect the stereochemistry of the original ion solution. Several other procedures designed to preserve the stereochemistry at C_4 and C_5, including the attempted oxidation of the ions in solution or the quenching of the solution with sodium borohydride or bromine, did not give usable results. An added problem arises in these latter cases because converting C_1 to an sp^3 center would allow for four geometric isomers.

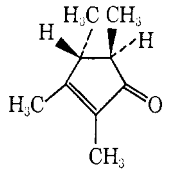

VIII


IX (*cis* or *trans*)

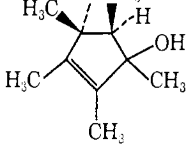
Proof of Structure of the Ions. As explained previously, a classical degradation of a recovered neutral compound was not possible as a method of structure proof for the ions. Further, the nmr spectra are not sufficiently distinctive to permit an analysis of the expected coupling constant differences. The equilibrium ratio of the two ions is highly suggestive, but it was considered desirable to obtain an unambiguous synthesis of the two ions.

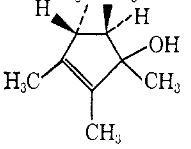
The synthesis of 2,3,4,5-tetramethylcyclopent-2-enone (X) has been reported.[14] This work was repeated and it was found that two isomeric ketones, separable by preparative glpc, are actually formed. These must be the corresponding *cis* (XA) and *trans* (XB) isomers, and once again, the ratio of the two ketones, *ca.* 15–85, is highly suggestive of their stereochemistry, since the experimental conditions would be likely to produce the equilibrium concentrations of the two. Two approaches were used.


XA


XB

1. The two ketones were *both* chemically degraded to either *dl*- or *meso*-2,3-dimethylsuccinic acid. The crude acids from the degradation were also esterified with diazomethane and analyzed by glpc. As expected, the major ketone (the lower boiling isomer) has the *trans* structure XB. The *cis* and *trans* ketones were then quantitatively converted to the corresponding alcohols, XIA and B, with methyllithium and these, on adding to chlorosulfonic acid at −80°, gave high percentages of the respective *cis* and *trans* isomeric carbonium ions, VIA and B.


XIA


XIB

2. The ketones were resolved using *l*-menthylhydrazide.[15] These were converted to the alcohols with methyllithium, as above. The *trans* isomer, XIB (active), would be expected to give an optically active carbonium ion whereas the *cis* isomer, XIA (active), would become inactive as an ion. However, the ion solutions are sufficiently colored and also scatter enough light so that the o.r.d. results are questionable. The ion from the *trans*-alcohol did, however, appear to have a small optical activity. Part of the difficulty in obtaining a large rotation could be explained by a photochemically produced (from the o.r.d. light source) racemization. The suprafacial shift of a proton from C_4 to C_1 in VI is photochemically allowed[16] and would result in a *d* ⇆ *l* interconversion without necessarily

d(or *l*) *l* (or *d*)

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[13] Unpublished results from this laboratory.

[14] L. de Vries, *J. Org. Chem.*, **25**, 1838 (1960).

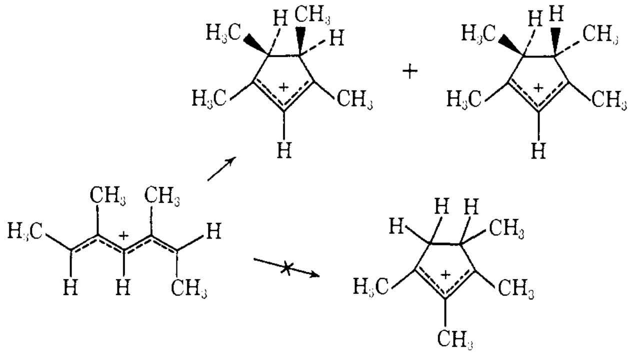
[15] (a) R. B. Woodward, T. P. Kohmar, and G. C. Harris, *J. Am. Chem. Soc.*, **63**, 120 (1941); (b) H. Sobotka, E. Bloch, H. Cahnmann, E. Feldbau, and E. Rosen, *ibid.*, **65**, 2061 (1943).

[16] R. B. Woodward and R. Hoffmann, *ibid.*, **87**, 2511 (1965).

isomerizing *via* the *cis* isomer or the cyclopentadiene (VIII).

Discussion

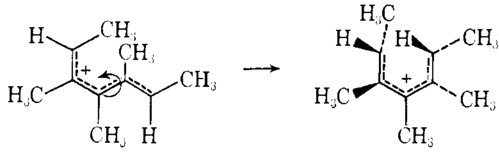
An examination of the data in Table I shows that the stereospecificity of the reaction, both in kind and in purity, is a variable of the acid solvent and the stereochemistry of the alcohol. The method of preparation is also important. It is clear however, that in general, the *cis–trans* alcohol VIIB gives a *preponderance of the cis cyclic ion* while the alcohols with the *cis–cis* and *trans–trans* geometry give *predominantly the trans cyclic ion.* The reaction is at best only 94% stereospecific and the reasons for the nonquantitative nature of the reaction are of some interest. Several factors could be involved: (1) orbital overlap considerations may not completely determine the reaction path, (2) isomerization might occur at the dienylic ion stage, or (3) isomerization could occur after cyclization. The first point cannot be tested in any satisfactory way. If one compares this system with the somewhat analogous octatriene cyclizations studied by Marvell, *et al.*, and by Vogel, *et al.*,[17] and for which complete stereospecificity is reported in some instances, then there is certainly no reason why this should not be so in the cases at hand. Similarly, point 3 is difficult to evaluate. Once formed in these strong acid solvents, there is no detectable change in the *cis/trans* ratio, except for the cases already discussed. What cannot be discounted is the possibility of hydride shifts occurring in the initially formed cyclic ion (which may be vibrationally excited). Information is, however, available from the tetramethyl series (corresponding to V), where hydride shifts would yield besides the *cis* and *trans* cyclic ions, yet a third isomer.[13] Under carefully controlled conditions, this ion *is not* produced, even though the *cis* and *trans* isomers are *both* present. We believe that isomerization is most likely at the dienylic ion stage and that this isomerization competes with the W, sickle, and U-shape "conformational" changes. Support for this mechanism comes from the data obtained for the alcohols VIIA and C, the former always giving much more stereospecific ring closures. The stability of each dienylic ion in the W, sickle, and U-shape conformations can be estimated by noting the number of *cis*-1,5-hydrogen interactions, *cis*-1,5-hydrogen–methyl interactions, or *cis*-1,5-methyl–methyl interactions (see formula V and notation below the structures), these being progressively more serious in increasing order. The effect of these interactions on the planarity (and hence the stability) of dienylic ions has been discussed.[2] The predicted stability order is VA > B > C. This analysis results in two conclusions. (1) The ion VC should have a higher transition state energy as compared to VA. A slower rate of cyclization would result in more opportunity for isomerizations to occur, and (2) statistically, the chances are overwhelming for an initial conversion of VC to the isomer VB, which on cyclization will yield the *opposite* stereochemistry.



Further support for these arguments comes from an examination of the data for the trifluoromethylsulfonic acid system. These data are unusual in two respects: (1) the alcohol VIB gives more *trans* than *cis* cyclic ion, even at −40°, and (2) the ratio of the *trans/cis* cyclic ion in the case of alcohol VIC *increases* with increasing temperature. These facts can be rationalized if the dienylic ion VB is converted before cyclization into >50% VA and if VC is partly converted first into VB which in turn gives VA. If this second conversion increases with temperature, then the reaction will appear to become more stereospecific. Why this solvent should be particularly good at promoting the interconversions is not known; however, these isomerizations could well involve the counterion in σ-bond formation.

It should be pointed out that K equilibrium for the two cyclic ions is about 20% *cis*, 80% *trans*, so that initial ratios near this value cannot be unambiguously evaluated. The fact that in all cases conditions occur where considerably more than 20% of the *cis* isomer is present, particularly at the higher temperatures, leads one to suspect that all of these reactions are kinetically controlled.

Other Possible Mechanisms. A cogwheel type process (shown below) in each case predicts the same stereochemistry as that predicted by the Woodward–Hoffmann rules. During rotation the hydrogen would tend to push the methyl group down and thereby give a transition state more favorable for forming the *cis*-cyclic ion. However, the isomer VA would seem to offer only a small steric barrier and this isomer is as stereospecific, or more so, compared to the others. It had been hoped that one could study the photochemical ring closures to ascertain whether the predicted opposite stereochemistry would be formed, but of course the thermal reaction is too rapid.



Experimental Section

Melting and boiling points are uncorrected. Ultraviolet spectral measurements were made using a Perkin-Elmer Model 202 spectrophotometer. Infrared measurements were made in dilute carbon tetrachloride solution using a Perkin-Elmer Model 337 spectrophotometer and can be obtained on request. Gas chromatography separations were made on one of several columns: (A) 6 ft × $^{1}/_{8}$ in. 5% SE-30 on Chromosorb W; (B) 12 ft × $^{3}/_{8}$ in. 30% Carbowax 20M on Chromosorb 60–80; (C) 12 ft × $^{3}/_{8}$ in. 30% Zonyl E-7 on Chromosorb 60–80. The nmr spectra of all neutral compounds were obtained as *ca.* 10% solutions in carbon tetrachloride using a Varian Associates A-60 or HA-100 nmr spectrometer. Values are reported in τ units. The optical rotatory dispersion measurements were made on a Jasco Model ORD/UV-5 spectropolarimeter.

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[17] (a) E. N. Marvell, G. Caple, and B. Schatz, *Tetrahedron Lett.*, 385 (1965); (b) E. Vogel, W. Grimme, and E. Dinne, *ibid.*, 391 (1965).

trans-2-Bromobut-2-ene was prepared as described[11] in approximately 95% geometric purity, bp 81° (650 mm). *cis*-2-Bromobut-2-ene was prepared as described,[11] except that a slight vacuum was applied during the dehydrohalogenation step in order to remove the bromoalkene from the reaction flask as quickly as it was formed. The crude product was washed with water, dried over anhydrous calcium chloride for 15 min, and used immediately without distillation. The geometric purity was usually about 95% and the yield about 80%.

3,4,5-Trimethylhepta-2-*cis*-5-*cis*-dien-4-ol (VIIA). The preparation of the vinyllithium reagents was carried out at ice-bath temperatures under an argon atmosphere, using lithium ribbon containing 1% sodium and ether as solvent. In almost every case, the reaction started quickly and proceeded smoothly. An ether solution of 3-methyl-3-penten-2-one was then added dropwise to the ice-cold vinyllithium solution and the mixture stirred for 1 hr at this temperature. The mixture was decanted through a glass wool plug into an ice–ammonium chloride solution and stirred until all of the solid had dissolved. The layers were separated and the aqueous layer was extracted with four 100-ml portions of ether or pentane. The combined organic layers were washed three times with carbonate solution and then dried over potassium carbonate. The residue was distilled to yield the crude alcohol, bp 82–84° (12 mm). In a typical preparation, from 45 g (0.33 mole) of bromobutene, 5 g of lithium, and 31.5 g (0.32 mole) of the ketone, there was obtained 37 g of alcohol, 75% yield. Redistillation of this material using an annular spinning band column gave a very pure fraction, bp 84° (12 mm), obtained from the latter part of the distillation, since the isomeric alcohols are lower boiling, n^{24}D 1.4757. *Anal.* Calcd for $C_{10}H_{18}O$: C, 77.92; H, 11.68. Found: C, 77.78; H, 11.96. Nmr analyses (60 mc) showed 4.46 (2 H, quartet of quartets, J = 6.6 and 1.1 cps, H at C_2 and C_6), 8.40 (6 H, doublet, J = 6.6 cps, each doublet split into approximately quartets, J = 1 cps, methyl of C_1 and C_8), 8.57 (6 H, quartet or quintet, $J \sim 1.1$ cps, methyls at C_3 and C_5), 8.71 (3 H, methyl at C_4). The alcohol OH peak is variable depending upon the concentration and can be hidden by the methyl proton signals.

3,4,5-Trimethylhepta-2-*cis*-5-*trans*-dien-4-ol (VIIB). From 31.5 g (0.32 mol) of the above ketone, 45 g (0.33 mol) of the *trans*-vinyl bromide, and 5 g of lithium, there was obtained 35 g (70%) of the crude alcohol, bp 81–84°. Redistillation using the annular spinning band column gave a fraction, bp 81° (12 mm), which is from the early part of the distillation, since the impurity is VIIA, n^{24}D 1.4734. *Anal.* Calcd for $C_{10}H_{18}O$: C, 77.92; H, 11.68. Found: C, 76.62; H, 11.99. Nmr analysis (60 mc) showed 4.47 (1 H, quartet of quartets, J = 6.6 cps and J = $\sim$1 cps (unsymmetrical), H at C_2), 4.76 (1 H, quartet of quartets, J = 6.6 cps and 1.2 cps, H at C_6), 8.37 (hint of splitting and 8.43, two overlapping quartets?, 12 H, methyl groups of C_1 and C_8 and at C_3 and C_5), 8.64, (3 H, methyl at C_4). The OH peak is variable.

3,4,5-Trimethylhepta-2-*trans*-5-*trans*-dien-4-ol (VIIC). From 15 g (0.17 mol) of ethyl acetate, 45 g (0.33 mol) of the *trans*-vinyl bromide, and 5 g of lithium, there was obtained 19.5 g (39%) of the crude alcohol, bp 75–81° (12 mm). Redistillation using the annular spinning band column gave a fraction, bp 76° (12 mm), which was redistilled a second time to give a fraction of about 97–98% (by nmr) purity. The impurity is VIIB. This alcohol is the lowest boiling of the three and the best fractions were the early ones, n^{24}D 1.4737. *Anal.* Calcd for $C_{10}H_{18}O$: C, 77.92; H, 11.68. Found: C, 77.82; H, 11.87. Nmr analysis (60 mc) showed 4.79 (2 H, quartet of quartets, J = 6.6 cps and *ca.* 1 cps (unsymmetrical), the protons at C_2 and C_6), 8.25 (*ca.* 6 H, quintet or two overlapping quartets, J = 1.5 cps, the methyl groups at C_3 and C_5), 8.42 (3 H, doublet, each split into quartets, J = 6.6 and 1.5 cps, the methyl groups of C_1 and C_8); 8.71 (3 H, the methyl at C_4). The OH peak is variable. There is an indication in this spectrum that the C_4-methyl protons are being coupled to others in the molecule with $J \sim$ 0.3 cps. Attempts to crystallize the alcohols were unsuccessful as were attempts to prepare crystalline derivatives.

Analysis of the Purity of the Alcohols (VIIA, B, C). The nmr peaks at τ 8.71 in VIIA and C and τ 8.64 in VIIB can be used to check the purity of the alcohols, since VIIA and C do not occur together. This latter result is expected because of the synthetic sequence used but was substantiated by using the τ 4.46 and 4.79 regions, for the analysis of these two alcohols.

2,3,4,5-Tetramethylcyclopent-2-enone (X). The synthesis of this ketone has been reported[14] but no mention was made of the stereochemistry involved. This synthetsis was repeated in good over-all yield to give a mixture containing *ca.* 80% of the *trans* isomer, XB, and 20% of the *cis* compound, XA. The lower boiling *trans* isomer can be separated pure by careful distillation through a spinning band column, bp 80° (13 mm), but the *cis* isomer slowly isomerizes during the extended refluxing involved and could not be obtained pure in this manner.

***trans*-2,3,4,5-Tetramethylcyclopent-2-enone** (XB). The constants for this ketone are: λ_{max} (methanol) 242 mμ, (ϵ_{max} 1.1 × 10^4); ir C=O at 1698 cm^{-1}, C=C at 1649 cm^{-1}; nmr (60 mc) 7.4–7.9 (broad), and 8.05–8.3 (a complex series of peaks, the protons at C_4 and C_5), 8.03 (3 H, methyl at C_3), 8.40 (3 H, multiplet, the methyl at C_2), 8.82 and 8.93 (6 H, two overlapping doublets, J = 6.6 cps, the methyl groups at C_4 and C_5). *Anal.* Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.12; H, 10.21.

***cis*-2,3,4,5-Tetramethylcyclopent-2-enone** (XA). The separation of this ketone was carried out by preparative glpc, column A, 120°, He flow 100 ml/min, the *trans* and *cis* ketones have retention times of 6.7 and 9.1 min, respectively: λ_{max} (methanol) 240 mμ (ϵ_{max} 1.2 × 10^4); ir C=O at 1699 cm^{-1}, C=C at 1655 cm^{-1}; nmr (60 mc) 7.3 (1 H, quartet, J = 7 cps, each peak of which appears to be split further into quartets, $J \sim$ 2 cps, the proton at C_4), 7.55, 7.66, 7.78 (1 H, part of a quartet?, J = 7 cps, the proton at C_5), 8.03 (3 H, broad, the methyl at C_3), 8.37 (3 H, septet, the methyl at C_2), 8.87 (6 H, doublet, J = 7 cps, the C_4 and C_5 methyl groups). *Anal.* Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.33; H, 10.56.

Degradation of *trans*-2,3,4,5-Tetramethylcyclopent-2-enone (XB). A stream of ozone was passed through a mixture of 0.276 g (0.002 mole of the ketone and 0.256 g (0.002 mole) of tetracyanoethylene[18] in 50 ml of ethyl acetate cooled to −70°, until the blue color of ozone persisted. The ethyl acetate was removed to yield a yellowish liquid and a solid. Carbon tetrachloride (10 ml) was added to the mixture, filtered, and the solid washed with three 10-ml portions of carbon tetrachloride to yield 0.280 g of pale yellow solid (TCE oxide). The combined carbon tetrachloride solution was flash evaporated to give 0.270 g of oil which was dissolved in 20 ml of 20% potassium hydroxide, with the aid of a few milliliters of dioxane, and treated with bromine at 0° until the bromine color persisted. The excess bromine was removed (sodium sulfite solution) and the solution strongly acidified with concentrated hydrochloric acid and continuously extracted with ether for 15 hr. Removal of the ether gave 0.200 g of brownish solid which was repeatedly recrystallized from benzene (charcoal) to give 0.120 g of white solid, mp 116–118° (sealed capillary) (lit.[19] mp 119.5–122° for *dl*-2-3-dimethylsuccinic acid).

Degradation of *cis*-2,3,4,5-Tetramethylcyclopent-2-enone (XA). The degradation was carried out as for XB, 0.552 g (0.004 mole), using a ketone mixture consisting of 72.7% of the *cis* isomer. Recrystallization of the crude acid (0.450 g) from hot water gave 0.160 g of yellow solid which was further recrystallized from benzene to give a white solid, mp 194–197.5° (sealed capillary) (lit.[19] mp 192–195° for *meso*-2,3-dimethylsuccinic acid). More acid was obtained by evaporating the water filtrate.

Glpc Analysis. The crude acids from the bromoform reaction were also esterified with diazomethane to give the crude liquid dimethyl esters. The two esters are separated on column C, operating at 165°, He flow of 100 ml/min, with retention times of 25.2 and 28.7 min. The low retention compound is the *meso* isomer, determined by comparison with an authentic sample. From degradation of XA, a mixture of 82.5% of the *meso* and 17.5% of the *dl* isomer was obtained, these percentages approximating those of the ketone mixture used. The *trans* ketone similarly gave the essentially pure *dl* ester.

1,2,3,4,5-Pentamethylcyclopent-2-en-1-ol (Methyls 4 and 5 *cis*) (XIA). A solution of 0.140 g (0.001 mole) of the ketone XA in 5 ml of ether was methylated with 1 ml (0.002 mole) of 2.1 *M* ethereal methyllithium at 0°, hydrolyzed with cold carbonate solution, and the ether solution separated. The aqueous solution was extracted twice with ether and the combined extracts dried over anhydrous potassium carbonate to give, after removal of the ether, 0.142 g of pale yellow, viscous liquid. Nmr analysis (100 mc) showed 9.09 and 9.03 (6 H, two doublets with $J \sim$ 7 cps), 8.86 (3 H, methyl group at C_1), 8.42 (6 H, broad, methyls at C_2 and C_3), $\sim$8 (multiplet, hydrogens at C_4 and C_5 and perhaps the OH peak). The compound is presumably a mixture of isomers about C_1.

Carbonium Ion from XIA. The above alcohol, 0.026 g, in 80 μl of deuteriochloroform was added to 0.5 ml of chlorosulfonic acid, which was cooled to −65° and vigorously stirred during the

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(18) R. Criegee and P. Gunther, *Ber.*, **96**, 1564 (1963).

(19) L. Eberson, *Acta. Chem. Scand.*, **13**, 40 (1959).

addition. The nmr spectrum of the ion solution indicates the presence of 87% of the *cis* ion VIA and 13% of the *trans* ion VIB. The alcohol XIA contains *ca.* 15% of the dehydration product, 1,2,3,4,5-pentamethylcyclopentadiene which, from separate experiments,[13] protonates to give *ca.* 60% *cis* (VIA) and 40% *trans* (VIB) cyclopentenyl cations. The above solution was diluted with chlorosulfonic acid for the ultraviolet spectral measurements.

1,2,3,4,5-Pentamethylcyclopent-2-en-1-ol (Methyls 4 and 5 *trans*) (XIB). An ether solution of the ketone XB, 0.300 g (0.022 mole), was methylated as for XIA to give 0.305 g of viscous oil. Nmr analysis (100 mc) showed 9.05 and 9.03 (two closely spaced doublets, $J \sim 7$ cps, the methyl groups at C_4 and C_5, 8.88 (3 H, methyl at C_1), 8.50 and 8.47 (methyl groups at C_2 and C_3, the C_4 and C_5 protons appear as a multiplet centered at $\sim$8.15). The compound is probably a mixture of isomers about C_1.

Carbonium Ion from XIB. In a preparation similar to that described above, using XIA, there was obtained an ion solution indicating 93% of the *trans* isomer, VIB, and 7% VIA. The solution was diluted for the ultraviolet spectral measurements.

***trans*-2,3,4,5-Pentamethylcyclopent-2-enone *l*-Menthylhydrazone.** The ketone, XB, 1.38 g (0.01 mole), and 2.13 g (0.01 mole) of *l*-menthylhydrazide[15] were added to 8.0 ml of an ethanol solution containing 2% sodium acetate and 1% acetic acid. The resulting solution was refluxed for 10 hr. Fractional crystallization from ethanol–water produced three compounds plus recovered *l*-menthylhydrazide: (1) mp 122–24°, (2) mp 140–41°, (3) mp 164–65°. Compounds 1 and 2 are derivatives of the ketone but compound **3** (from nmr and CHN analysis) appears to be a reaction product of the hydrazide. Compound **1** was obtained in the larger amounts and was therefore used for the recovery of the ketone. *Anal.* Calcd for $C_{20}H_{34}N_2O_2$ (compound **1**): C, 72.3; H, 9.6; N, 8.4. Found: C, 72.08; H, 9.82; N, 7.99. The rotation in methanol was $[\alpha]^{25}\mathrm{D} \sim -100$.

Decomposition of the Hydrazone and Attempted Preparation of Optically Active Carbonium Ion. The hydrazone, 0.97 g (0.0029 mole), was added to a solution of 21 ml of water and 2.7 g of phthalic anhydride and the mixture subjected to steam distillation (1.5 hr). The distillate was extracted with three 50-ml portions of ether and the ether solution dried over magnesium sulfate. Removal of the ether left 0.32 g of colorless liquid. This liquid consists of the *cis* and *trans* ketones, XA and B, in a ratio of 1:6.9. These were separated by preparative glpc as previously described. The *trans* ketone has an $[\alpha]^{25}\mathrm{D} \sim -20$ and shows a negative Cotton curve with two minima at 348 and 354 mμ, respectively. The *cis* ketone was obtained in too small an amount to measure the rotation but should also be active since *cis–trans* isomerization of the ketones should not cause racemization. The corresponding alcohols were made as previously described. The carbonium ions from these alcohols were prepared in chlorosulfonic acid solution but were yellowish orange in color, somewhat cloudy and did not give rotations large enough to unambiguously separate from base line drift, etc.

Cryoscopic Measurements. The apparatus consisted of an inner pear-shaped three-necked flask with an outer air jacket surrounding this. The top joint was fitted with a Beckman thermometer having a 24/40 joint and one of the side joints was fitted with a microstirrer which seals into a 24/40 joint. A serum cap was fitted over the third outlet. The alcohols were added from a microliter syringe through the serum cap, to weighed amounts of 100% sulfuric acid, during a period of rapid stirring. About five to eight points were obtained in a typical experiment. Calibration runs were performed using acetone as the solute.

Recovery Experiments. These were performed as previously described,[2] using *ca.* 5-g amounts of the alcohols in 100 g of 96% sulfuric acid. The hexane extraction method was used to prepare the ion solution. A 90% recovery of monomeric hydrocarbons could usually be obtained. The crude recovered dienes were fractionated using a spinning band column to give 1,2,3,4,5-pentamethylcyclopentadiene (VIII), bp 58° (10 mm), in about 75% yield. The forerun consists of exocyclic diene(s) which make up about 8% of the total recovered compound (from glpc analysis). Nmr analysis of VIII (60 mc) showed 7.67 (1 H, quartet, $J = 7.8$ cps, proton at C_5), 8.31 (12 H, methyl groups at C_1, C_2, C_3, and C_4), 9.10 (3 H, doublet, $J = 7.8$ cps, methyl group at C_5). This compound has been previously prepared by another method.[14] The presence of the exocyclic isomers (IX) in the forerun is clearly shown by the characteristic nmr signals at 5.5 and 5.6 ($=CH_2$).

Preparation of the Ions. Sulfuric acid concentrations were determined by titration. Fluorosulfonic acid, antimony pentafluoride, trifluoromethylsulfonic acid were purified by double distillation. Chlorosulfonic acid (commercial B.D.H.) was used as is[20] and a solution of the anhydride of chlorosulfonic acid in chlorosulfonic acid was prepared and analyzed as described.[20] All ion solutions employing sulfuric acids were made using the hexane extraction procedure. With chlorosulfonic acid, trifluoromethylsulfonic acid, fluorosulfonic acid, and the two mixtures based on these, a number of techniques were tried, ranging from the straight addition of the alcohol from a microliter syringe to the use of solutions of varying concentrations. Solvents tried were sulfur dioxide, carbon tetrachloride, deuteriochloroform, methylene chloride, and perfluoroalkane compounds. The time for the additions, the rate of stirring, and the drop size were also varied. The averaged data are reported in Table I. In general, the ratios, with or without solvents, are reasonably similar. The temperature during the addition is a more important variable. All solutions were made to *ca.* 10% weight of alcohol/volume of solvent, and were prepared on a 0.5–1-ml scale in most cases.

Measurement of the Ion Ratio. The individual nmr peaks for the *cis* ion (VIA) and the *trans* ion (VIB) are reported in Table II. The ratio measurements were carried out on the C_4- and C_5-methyl region of the spectrum using *both* 60- and 100-mc spectra (Figure 1). In the 60-mc spectra, the areas of the second peaks of each doublet were measured, both by tracing and weighing curves and by peak height measurements. The latter measurement was corrected by multiplying each height by the half-width at half-height value for each curve. In the 100-mc spectra, the first peak of the first doublet and the last peak of the second doublet were used for the analysis. The actual measurements were made from spectra recorded at 100- or 250-cps sweep widths.

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(20) E. A. Robinson and J. A. Ciruna, *Can. J. Chem.*, **46**, 1720 (1968).