The Effect of Substitution on Homoallenic Participation in Solvolyses[1]

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Abstract: Eight β-allenic alcohols were synthesized and the tosylate and brosylate [3,5-dinitrobenzoate (VIe) in the case of 2-methyl-4,5-heptadien-2-ol] of each prepared. The rates of acetolysis (hydrolysis in the case of VIe) were determined titrimetrically. Solvolysis products were isolated and their structures assigned on the basis of spectra and properties. Each compound studied except VIe, exhibited a significant k_Δ (assisted solvolytic rate) when compared to the saturated analog. The fact that VIe underwent hydrolysis only one-third as fast as 2-methyl-2-butyl 3,5-dinitrobenzoate is attributed to the rate-retarding inductive influence of the allene moiety. It was observed that 4,5-hexadien-2-yl tosylate (Ib) rapidly rearranged during acetolysis, but all other substrates could be recovered unchanged after partial acetolysis. The fraction of cyclized or rearranged solvolysis products ranged from 0% for VIe to 100% for esters of 2,2-dimethyl-3,4-hexadienol (Va). The results are interpreted as evidence for homoallenic anchimeric assistance in the transition states for solvolysis; the intermediates have been formulated as bicyclobutonium ions except in the case of VIe.

Although a large body of literature has accumulated dealing with the phenomenon of homoallylic participation,[3] only recently has the ability of a β-allenic system to participate in solvolyses been examined. Bertrand and Santelli reported[4] that hydrolysis of 4,5-hexadien-2-yl *p*-toluenesulfonate (tosylate) (Ib) led to 67% *cis*- and *trans*-2-methylcyclopropyl methyl ketones and 30% unrearranged 4,5-hexadien-2-ol (Ia). Similar treatment of 4-methyl-4,5-hexadien-2-yl tosylate gave a mixture containing 67% *cis*- and *trans*-1,3-dimethyl-2-methylenecyclobutanols, 17% 1,4-dimethyl-2-methylenecyclobutanol, and 16% unrearranged alcohol. Later these authors found[5] that hydrolysis of optically active Ib gave the cyclic ketones with activity retained, but the isolated alcohol (Ia) was completely racemic.

It has also been reported[6] that, under a variety of solvolytic conditions, β-naphthalenesulfonates of 3,4-pentadien-1-ol (IIa) and 3,4-hexadien-1-ol (IIIa) yielded substantial amounts of alkyl cyclopropyl ketones, together with hydrocarbons, acetates of the unrearranged alcohols, and unidentified compounds in varying amounts. Unfortunately the lack of definitive kinetic data did not permit these authors to detect homoallenic participation in the transition states of these solvolyses, nor was it possible to decide whether nonclassical carbonium ion intermediates were involved.

Finally, Bly and coworkers have reported[7] that acetolysis of 2,2-dimethyl-3,4-pentadien-1-yl *p*-bromobenzenesulfonate (brosylate) yielded a mixture comprising 2-methyl-4,5-hexadien-2-yl acetate (77%), and the related hydrocarbons 2-methyl-1,4,5-hexatriene (12%) and 2-methyl-2,4,5-hexatriene (11%). Noticeably absent were products with unrearranged carbon skeleton such as 2,2-dimethyl-3,4-pentadien-1-yl acetate, and cyclic products such as 2,2-dimethylcyclopropyl methyl ketone. Similarly absent were any products, such as 3-methyl-4,5-hexadien-3-yl acetate, which would have arisen from methyl migration, a rearrangement commonly encountered in the solvolysis of neopentyl compounds.[8] Ethanolysis and hydrolysis of the brosylate gave the related rearranged ether and alcohol, respectively, together with the hydrocarbons.

Comparison of the kinetics of this acetolysis with those of the related homoallyl and saturated neopentyl compounds (Table VI) clearly indicated homoallenyl participation in the transition state of the rate-determining step. These comparisons were made even more striking by including an estimate of the rate-retarding inductive effect of the allenyl group compared to that of the saturated group. These data were interpreted as evidence for a delocalized transition state which opened to a product-determining classical ion. It was mentioned that the *gem*-dimethyl group not only inductively stabilized the rearranged classical ion, but also aided in the formation of the bridged transition state.

Thus, although there have been several examples of the intervention of a β-allenic system in solvolytic reactions, the widely varied conditions under which these observations have been made make meaningful comparisons and generalizations difficult. It was the purpose of the present work to reexamine the solvolytic reactivities of the key compounds mentioned so far, together with some additional compounds, under a fixed set of conditions, then compare the results with suitable saturated model compounds and homoallylic systems to assess the significance and generality of homoallenic participation.

Syntheses. The eight β-allenic systems I–VIII were prepared for study. Syntheses given in the literature were used for Ia,[4] IIa,[6] IIIa,[6] and Va;[9] IVa was pre-

(1) Abstracted from the Ph.D. Thesis of Roger S. Macomber, University of California, Los Angeles, 1968. For a preliminary report of part of this work, see T. L. Jacobs and R. Macomber, *Tetrahedron Letters*, 4877 (1967). This research was supported by grants from the National Science Foundation.

(2) National Science Foundation Graduate Trainee, 1966–1968.

(3) For an excellent reprint collection and commentary, see P. D. Bartlett, "Nonclassical Ions," W. A. Benjamin, Inc., New York, N. Y., 1965.

(4) M. Bertrand and M. Santelli, *Compt. Rend.*, **259**, 2251 (1964).

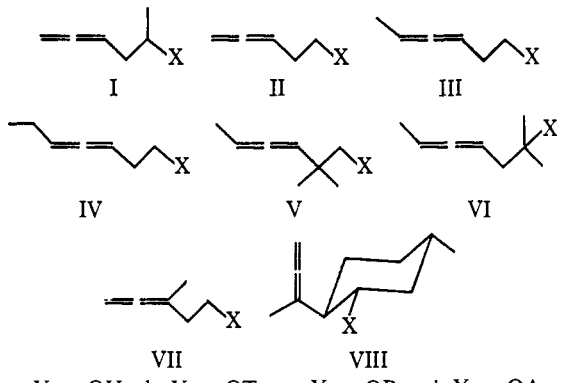
(5) M. Bertrand and M. Santelli, *Chem. Commun.*, 718 (1968).

(6) M. Hanack and J. Haffner, *Tetrahedron Letters*, 2191 (1964); *Chem. Ber.*, **99**, 1077 (1966).

(7) R. S. Bly, A. R. Ballentine, and S. U. Koock, *J. Am. Chem. Soc.*, **89**, 6993 (1967); R. S. Bly and S. U. Koock, *ibid.*, **91**, 3292, 3299 (1969).

(8) For example see R. D. Guthrie, *ibid.*, **89**, 6718 (1967).

(9) T. L. Jacobs, R. Macomber, and D. Zunker, *ibid.*, **89**, 7001 (1967).

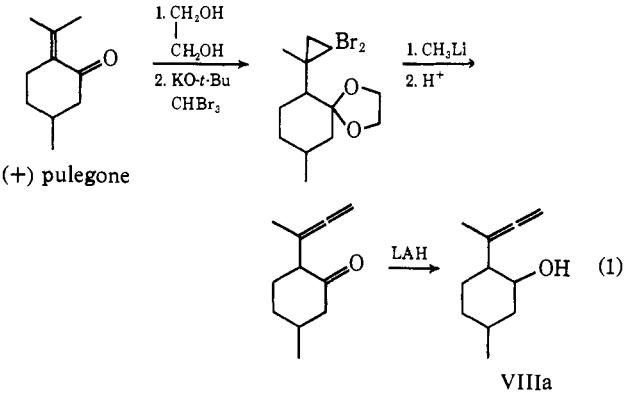


a, X = OH; b, X = OTs; c, X = OBs; d, X = OAc; e, X = 3,5-dinitrobenzoate

pared by a sequence analogous to that for IIIa. Because acetolysis of 2,2-dimethyl-3,4-hexadien-1-yl tosylate (Vb) led exclusively to esters of 2-methyl-4,5-heptadien-2-ol (VIa) and related hydrocarbons (*vide infra*), a solvolytic route was chosen for the synthesis of VIa. Because the tosylate of VIa could not be prepared, owing presumably to its high reactivity, the 3,5-dinitrobenzoate ester was synthesized for study.

The preparation of 3-methyl-3,4-pentadien-1-ol (VIIa) involved the addition of "dibromocarbene" to the tetrahydropyranyl ether of 3-methyl-3-buten-1-ol, reaction of the dibromocyclopropane with methyllithium, and hydrolysis. This probably represents the most general synthetic route to β-allenic alcohols, as it is limited only by the availability of the starting olefinic alcohol.

Finally, 5-methyl-2-(1-methylpropadienyl)cyclohexanol (VIIIa) was synthesized by the method of Bertrand and Santelli[10,11] (eq 1) in order to examine the



(+) pulegone

VIIIa (1)

possible effect of ring strain on solvolysis rates and products. These investigators did not discuss the stereochemistry of the cyclic alcohol. When the exocyclic double bond in pulegone is isomerized during formation of the ketal, the sterically favored isomer would be the one with the *trans* (diequatorial) arrangement of the methyl and 2-propenyl groups. This configuration should persist through to the allenic ketone. The question then arises, however, as to which epimer (–OH equatorial or axial) will result from attack of hydride at the carbonyl. It is often difficult to predict the epimeric constitution of such mixtures.[12] Product development control would favor equatorial –OH, but steric approach control often leads to axial –OH owing to the fact that equatorial approach of the hydride donor is favored over axial approach. However, examination of molecular models suggests that steric approach control should not be as important as the stability of the product.

Experimentally it was found that lithium aluminum hydride reduction of the allenic ketone afforded two isomers in the ratio 5:1. Spectral analysis of the mixture clearly indicated that the major component was the desired allenic alcohol. On the basis of the complex coupling of the proton geminal to the –OH, the product was assigned the equatorial configuration. The nmr absorption of this proton very closely resembled that of l-menthol,[13] which is known to possess the all-equatorial configuration.[14] The minor component of the mixture was apparently not the axial epimer, but rather the conjugated isomer, based on an infrared absorption at 1640 cm^{-1} and an ultraviolet absorption λ_{max} 255 mμ (log ϵ 3.57). The mixture could not be further separated, so succeeding studies were carried out with allowances made for the conjugated isomer. The conclusions drawn from the acetolysis of VIIIb should be considered tentative until both epimers have been isolated and studied separately.

Results

The rates of acetolyses of the allenic arenesulfonates, determined in anhydrous acetic acid buffered with sodium acetate and containing ~1% acetic anhydride, were followed titrimetrically as described in the Experimental Section. Rate constants were calculated on an IBM 360 computer, using the initial substrate concentration as opposed to the infinity titer method, because the former method is a more sensitive test for return to a less reactive substrate.[15] The titrimetric rate constants and associated activation parameters are given in Table I.

Generally, the plots of ln (C_0/C_t) *vs.* time were strictly linear to 70–90% completion, with the probable error in the values of the rate constants less than 1.5%. To estimate the sensitivity to added sodium acetate concentration, additional runs were made with double the original salt concentration. The results, listed in Table II, include an estimate of the *b* value for added sodium acetate, calculated from Winstein's equation for normal salt effects[16]

$$k = k_0(1 + \sum_i b_i c_i)$$

where k_0 is the apparent first-order titrimetric rate constant at zero ionic strength, and b_i is the numerical dependence of the titrimetric rate on c_i, the concentration of salt$_i$. The derived *b* values are typical for solvolyses in which anchimeric assistance may be important.[17]

It was discovered that compounds Ib and c exhibited very rapidly decreasing values of the integrated rate con-

(10) M. Santelli, *Compt. Rend.*, **261**, 3150 (1965).
(11) M. Bertrand and M. Santelli, *ibid.*, **262**, 1601 (1966).
(12) H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, Inc., New York, N. Y., 1965.
(13) "High Resolution NMR Spectra Catalog," Vol. I, Varian Associates, Palo Alto, Calif., 1962.
(14) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 220.
(15) K. L. Servis and J. D. Roberts, *Tetrahedron Letters*, 1369 (1967).
(16) A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, **78**, 2763 (1956).
(17) See, for example, R. K. Bly and R. S. Bly, *J. Org. Chem.*, **31**, 1577 (1966).

Table I. Titrimetric First-Order Rate Constants for Acetolyses of β-Allenic Arenesulfonate Esters[a]

Compd	Temp, °C	k_t, sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	$\Delta E^{\ddagger}$, kcal/mol	k_{rel}[b]	k_{Bros}/k_{Tos}
IIb	65.0	$(7.10 \pm 0.10) \times 10^{-7}$	25.0	−12.9	25.70 ± 0.05	1.00	
	85.2	$(6.07 \pm 0.05) \times 10^{-6}$					
	100.0	$(2.57 \pm 0.02) \times 10^{-5}$					
IIc	100.0	$(6.38 \pm 0.01) \times 10^{-5}$					2.48
IIIb	50.4	$(2.44 \pm 0.02) \times 10^{-7}$					
	65.0	$(1.59 \pm 0.01) \times 10^{-6}$	26.7	−6.3	27.40 ± 0.15	2.22	
	85.0	$(1.50 \pm 0.01) \times 10^{-5}$					
IIIc	85.1	$(4.82 \pm 0.02) \times 10^{-5}$					3.21
IVb	50.5	$(2.75 \pm 0.02) \times 10^{-7}$					
	65.0	$(1.57 \pm 0.01) \times 10^{-6}$	25.8	−9.2	26.42 ± 0.10	2.21	
	85.0	$(1.43 \pm 0.01) \times 10^{-5}$					
IVc	85.0	$(4.64 \pm 0.02) \times 10^{-5}$					3.24
Ib[c]	50.1	$(2.27 \pm 0.03) \times 10^{-6}$					
	65.0	$(1.16 \pm 0.02) \times 10^{-5}$	24.6	−8.5	25.29 ± 0.39		
	85.0	$(1.03 \pm 0.01) \times 10^{-4}$					
d	65.0	2.8×10^{-5}				39	
Ic[c]	85.0	$(3.23 \pm 0.02) \times 10^{-4}$					3.14
Vb	40.0	$(1.83 \pm 0.01) \times 10^{-5}$					
	50.0	$(5.96 \pm 0.02) \times 10^{-5}$					
	65.0	$(3.21 \pm 0.02) \times 10^{-4}$	23.5	−5.4	24.14 ± 0.12	452	
Vc	40.0	$(6.43 \pm 0.07) \times 10^{-5}$					3.51
	50.1	$(2.13 \pm 0.02) \times 10^{-4}$					3.58
	65.0	$(9.93 \pm 0.31) \times 10^{-4}$	22.4	−6.5	23.02 ± 0.27		3.10
VIe[e]	65.0	$(1.21 \pm 0.03) \times 10^{-6}$	19.9	−27	20.56		
	80.0	$(4.44 \pm 0.06) \times 10^{-6}$					
VIIb	65.0	$(1.64 \pm 0.01) \times 10^{-6}$	24.7	−12.1	25.39 ± 0.40	2.40	
	85.0	$(1.27 \pm 0.00) \times 10^{-5}$					
	100.0	$(5.73 \pm 0.06) \times 10^{-5}$					
VIIc	85.0	$(3.89 \pm 0.03) \times 10^{-5}$					3.07
VIIIb[f]	65.0	$(1.41 \pm 0.02) \times 10^{-5}$	25.7	−5.0	26.36	19.9	
	85.0	$(1.26 \pm 0.01) \times 10^{-4}$					

[a] $[ROSO_2Ar]_i \sim 0.10$ *M*; $[NaOAc] \sim 0.11$ *M*. [b] At 65° for tosylate. The quoted uncertainty in the apparent first-order rate constant is the *probable error* as defined in H. Margenau and G. M. Murphy, "Mathematics for Physics and Chemistry," D. Van Nostrand Co., New York, N. Y., 1956, p 519. [c] Returns to a less reactive substrate, giving a nonlinear plot. Value calculated to 30% reaction. See text. [d] Corrected for rearrangement. [e] For hydrolysis in 65% aqueous dioxane. [f] Calculated rate constants based on infinity titer rather than initial substrate concentration owing to impurity of substrate (see Experimental Section).

Table II. Effect of Added Acetate Ion on β-Allenic Tosylate Acetolysis

Compd	Temp, °C	k_t, sec^{-1} [a,b]	$[NaOAc]_i$	b_{NaOAc}
IIb	100.0	$(2.57 \pm 0.02) \times 10^{-5}$	0.1059	
		$(3.46 \pm 0.02) \times 10^{-5}$	0.2097	7.2
IVb	85.0	$(1.43 \pm 0.01) \times 10^{-5}$	0.1065	
		$(1.89 \pm 0.01) \times 10^{-5}$	0.2107	4.6
Ib[c]		$(1.03 \pm 0.01) \times 10^{-4}$	0.1066	
		$(1.42 \pm 0.01) \times 10^{-4}$	0.2109	7.5
Vb	65.0	$(3.21 \pm 0.02) \times 10^{-4}$	0.1090	
		$(3.00 \pm 0.03) \times 10^{-4}$	0.2025	−0.6
VIIb	85.0	$(1.27 \pm 0.00) \times 10^{-5}$	0.0986	
		$(1.57 \pm 0.01) \times 10^{-5}$	0.2013	3.0
VIIIb[d]		$(1.26 \pm 0.01) \times 10^{-4}$	0.1031	
		$(1.37 \pm 0.01) \times 10^{-4}$	0.1978	1.0

[a] $[ROTs]_i \sim 0.10$ *M*. [b] See footnote *b*, Table I. [c] See footnote *c*, Table I. [d] See footnote *f*, Table I.

stant with time and that after two "half-lives" no unrearranged tosylate could be detected. In order to estimate the true (*i.e.*, closer in value to the ionization rate constant) titrimetric rate constant, the assumption was made that it could be better approximated as the sum of the observed titrimetric rate constant for acetolysis of Ib (k_t) and the rate constant for return (k_r) to a substrate which was less reactive than the starting material. The magnitude of k_t (1.45×10^{-5} sec^{-1} at 65°) was determined by extrapolation of a plot of $k_{instantaneous}$ *vs.* time to $t = 0$. A crude estimate of the acetolysis rate constant of the rearranged tosylate was obtained by extrapolation of the same plot to $t \rightarrow \infty$; the value was $\sim 0.65 \times 10^{-5}$ sec^{-1}. The value of $k_r + k_t$ was determined as follows. Samples of Ib were allowed to undergo partial acetolysis for varying periods, then the unreacted tosylates were recovered. The relative amounts of rearranged and unrearranged sulfonates were determined by examination of the nmr spectrum of the mixture, and the data were reduced to kinetic form (see Experimental Section). A plot of ln (C_0/C_t) *vs.* time for disappearance of Ib was linear, with a rate constant of 2.8×10^{-5} sec^{-1} at 65°. Table I includes the "corrected" value for the acetolysis rate constant of Ib at 65°. Therefore, $k_r = (k_{disappearance} - k_t)$ has a value of 1.35×10^{-5} sec^{-1} at 65°.

Rate constants for hydrolysis of 3,5-dinitrobenzoate VIe (Table I) were measured in 65% (volume) aqueous dioxane by titrating liberated 3,5-dinitrobenzoic acid. Accumulation of 3,5-dinitrobenzoic acid in these unbuffered hydrolyses led to increasing values of the integrated rate constant with time, a positive salt effect of the type often encountered. Calculated rate constants had greater probable errors than with the acetolyses because of this effect and because the concentration of titrant base varied (daily standardization required). The uncertainty is somewhat greater with 2-methyl-2-butyl 3,5-dinitrobenzoate.

The behavior of the brosylate and tosylate of any given allenic alcohol was similar in all cases. The ratio of reactivities (k_{Bros}/k_{Tos}) generally had the expected value of 3.3 ± 0.2 (Table I).

Table III. Titrimetric First-Order Rate Constants for Acetolyses of Alkyl *p*-Toluenesulfonates[a]

Compd	Temp, °C	k_t, sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	$\Delta E^{\ddagger}$, kcal/mol
n-Pentyl	65.0[b]	3.73×10^{-7}	26.0	−11.5	26.63
	85.0	$(3.40 \pm 0.07) \times 10^{-6}$			
	100.0	$(1.53 \pm 0.02) \times 10^{-5}$			
n-Hexyl	65.0[b]	5.09×10^{-7}	24.0	−16.8	24.63
	85.0	$(3.94 \pm 0.04) \times 10^{-6}$			
	100.0	$(1.59 \pm 0.02) \times 10^{-5}$			
n-Heptyl	65.0[b]	3.84×10^{-7}	26.0	−11.3	25.95
	85.0	$(3.52 \pm 0.06) \times 10^{-6}$			
	100.0	$(1.59 \pm 0.02) \times 10^{-5}$			
2-Hexyl	65.0	$(2.36 \pm 0.01) \times 10^{-5}$	25.3	−5.3	25.93
	85.0	$(2.03 \pm 0.03) \times 10^{-4}$			
2,2-Dimethylhexyl brosylate	65.0[c]	1.93×10^{-7}			
2-Methyl-2-butyl	65.0[d]	$(3.62 \pm 0.12) \times 10^{-6}$			
3,5-dinitrobenzoate	80.0[d]	$(2.08 \pm 0.08) \times 10^{-5}$			
trans-4-Butylcyclohexyl	65.0[b]	1.01×10^{-5}			
tosylate	75.0[e]	3.75×10^{-5}			
	100.0[e]	6.14×10^{-4}			

[a] See footnote *a*, Table I. [b] Extrapolated. [c] Extrapolated from data in E. N. McElrath, R. M. Fritz, C. Brown, C. Y. LeGall, and R. B. Duke, *J. Org. Chem.*, **25**, 2195 (1964). [d] For hydrolysis in 65% (volume) aqueous dioxane. [e] Extrapolated from data in S. Winstein and N. J. Holness, *J. Am. Chem. Soc.*, **77**, 5562 (1955).

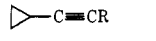
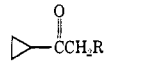
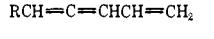
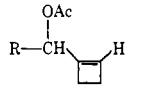
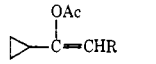
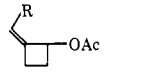
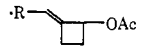
In order to assess the significance of homoallenic participation in the solvolysis transition state, it was also necessary to measure the solvolytic rates for judiciously chosen model compounds.[18] The models chosen were generally the saturated analogs of the allenic compounds. For VIIb and VIIIb the models were *n*-pentyl tosylate and *trans*-4-*t*-butylcyclohexyl tosylate, respectively. The results are given in Table III. As would be expected, the primary model compounds (*n*-pentyl, *n*-hexyl, and *n*-heptyl) showed greater sensitivity to the depletion of acetate ion, resulting in somewhat greater curvature in the plots of ln (C_0/C_t) *vs.* time. As a result, apparent first-order titrimetric rate constants were calculated to ~50% completion. The 3,5-dinitrobenzoate of 2-methyl-2-butanol was selected as a model for the hydrolysis of VIe, and its hydrolytic data are also given in Table III.

Each of the allenic tosylates was subjected to preparative acetolysis (hydrolysis in the case of VIe) carried to seven to ten half-lives. Preparative scale conditions were exactly the same as those for the kinetics investigation, except that the initial acetate ion and substrate concentrations were doubled to facilitate product isolation. The products were isolated, in most cases, by means of gas–liquid partition chromatography (glpc) and were identified on the basis of their ir, nmr, and mass spectra, elemental analysis, and comparison with known compounds (when available). Spectral data and structural assignments are given in the Experimental Section. Relative amounts of products were determined from crude analytical glpc peak areas. Each isolated product was rechromatographed as a test for isomeric purity and stability under the separation conditions. To ensure that the isolated products were indeed primary products, small amounts of the acetolysis mixture were removed after *ca.* one half-life and analyzed by glpc. Only if this early analysis differed significantly (>5%) from the later analysis, or if an obvious product was not observed were the isolated products more carefully examined for stability.

The ratios of acetolysis products for compounds IIb, IIIb, and IVb are given in Table IV. The results for the

(18) E. Kosower, "An Introduction to Physical Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1968, p 102.

Table IV. Acetolysis Products from RCH=C=CHCH$_2$CH$_2$OTs

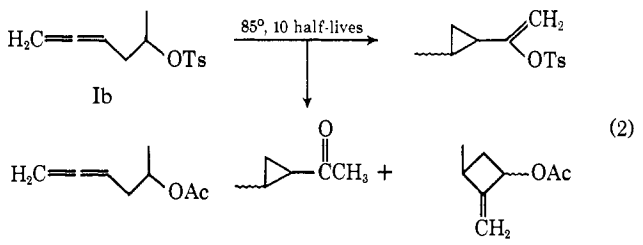
Product	R = H (IIb)[a]	R = CH_3 (IIIb)[b]	R = C_2H_5 (IVb)[c]
		31	28
	11	5	17
			4
		7	4
	3	8	4
	6	8	9
	(Ident)	27	16
RCH=C=CHCH$_2$CH$_2$OAc	76	14	12
RC≡CCH$_2$CH$_2$CH$_2$OAc			5

[a] 100°, seven half-lives, 4% unidentified. [b] 85°, ten half-lives. [c] 85°, ten half-lives, 1% unidentified.

first two of these are considerably more complicated than the earlier report[6] shows. Significant is the fact that enol acetates (and related acetylenes), which were postulated but not isolated by the previous workers,[6] were isolated here. In these three cases there was no evidence for return of the starting material to a rearranged sulfonate.

Allenic tosylate Ia gave the products shown in eq 2. The major product was unrearranged acetate Id even though Ia rearranged rapidly to a tosylate believed to have the cyclopropylvinyl structure shown. Further work will be carried out to see which products arise from rearranged tosylate and to examine the solvolysis with optically active Ib.[5]

Acetolysis of Vb and c gave three principal products (Table V). Unrearranged acetate Vd was not detected



among these, although a sample prepared directly from Va was stable under the reaction and separation conditions. If present, this ester must constitute less than 0.1% of the mixture, the limit of glpc sensitivity here. Two products were identified as 2-methyl-1,4,5-heptatriene (IX) and 2-methyl-4,5-heptadien-2-yl acetate (VId). The third component was rechromatographed, revealing it to be a mixture of three compounds in the ratio 5:2:1. Elemental analysis was in agreement with the empirical formula C_8H_{12}. A strong ir absorption at 1960 cm^{-1} was indicative of an allenic compound as the major component of the mixture. The identity of this compound is most likely 2-methyl-2,4,5-heptatriene (X) on the basis of the ultraviolet spectrum [λ_{max} 232 mμ (log ε 4)] and analogy with Bly's results.[7] A shoulder at 252 mμ suggests that the other components of the mixture may be 2-methyl- and 6-methyl-1,3,5-heptatriene; geometrical isomers are possible for both of these. The nmr spectrum of the mixture was in agreement with the proposed composition. Such trienes might arise from rearrangement of the allenic hydrocarbon products, although the composition of the mixture was essentially unchanged after subjection to acetolysis conditions and rechromatography. Although hydrocarbon IX was stable to the reaction and separation conditions, tertiary ester VId tended to eliminate acetic acid to form the hydrocarbons. An nmr spectrum of the crude acetolysis product mixture showed the ester in amounts up to 85–90%, but glpc always indicated lesser amounts. Similar difficulties were encountered by Bly.[19] Table V gives the product ratios from Vb and c as a function of time. It is clear as expected, that common intermediates are involved in both cases. Also significant is the fact that no products were detected which would have arisen from 1,2-methyl migration.

Table V. Acetolysis Product Ratios of 2,2-Dimethyl-3,4-hexadienyl Arenesulfonate Esters[a]

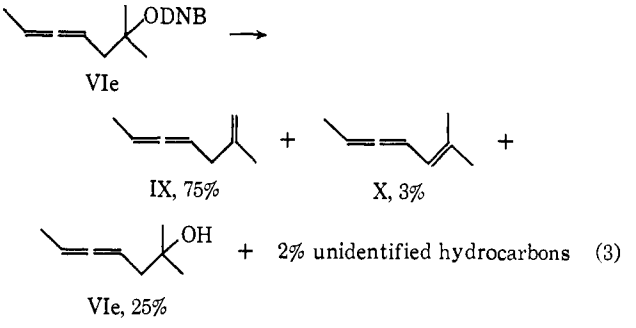
Compd	Reaction[b] period	VId	IX	X	Other[c]
Vb	5	49	23	18	10
	8	54	20	16	10
Vc	6	45	25	19	11
	10	55	16	18	11

[a] Temperature 65°; values from uncorrected glpc peak areas (see Experimental Section). [b] In half-lives. [c] Two components, probably conjugated trienes, in the ratio 2:1.

Acetolysis of optically active Vc, $[\alpha]^{25}D$ −2.7° (from (−)Va,[9] $[\alpha]^{25}D$ −6.6°), gave optically active IX and Vd, $[\alpha]^{25}D$ −2.6 and −3.9°, respectively. The hydrocarbon mixture (>60° X) was also active, $[\alpha]^{25}D$ −1.5°.

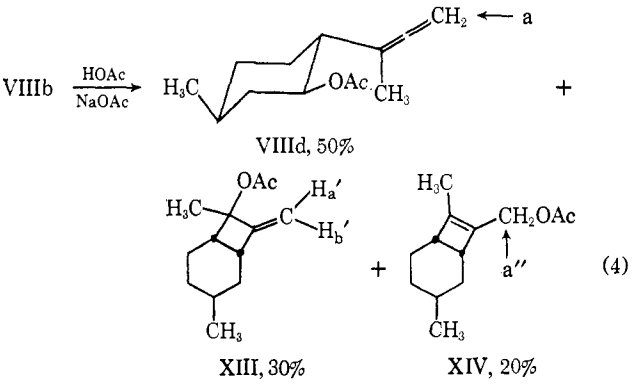
Hydrolysis of tosylate Vb in 50% aqueous acetone containing ~10% pyridine gave only rearranged products that would be expected by analogy with the acetolysis. As mentioned previously, this method was employed on a preparative scale for the synthesis of Va. Neither under acetolysis nor hydrolysis conditions was there any evidence for return of Vb or c to a rearranged sulfonate.

Hydrolysis of VIe in 65% aqueous dioxane led to four products (eq 3) which were not isolated; the glpc retention times of three of these were identical with times expected for unrearranged alcohol VIe and related hydrocarbons IX and X.



When VII was subjected to acetolysis conditions, and the product mixture analyzed by glpc, only two components appeared. These were separable by distillation, and the first was immediately identified as 1-methyl-2-methylenecyclobutyl acetate (XI). The second component exhibited a glpc retention time identical with that of authentic VIId, but the nmr spectrum indicated that the unrearranged ester comprised only 20%, while the major constituent was 1-acetoxymethyl-2-methylcyclobutene (XII). A study of the fraction of XI *vs.* reaction length indicates that XI is the major product, and that it slowly undergoes allylic rearrangement to XII (eq 6). This suggests that the related cyclobutenes from IIIb and IVb are also secondary products, *i.e.*, they arise by rearrangement of one of the primary products, probably the methylenecyclobutanes.

Cyclic allenyl tosylate VIIIb presented experimental difficulties in purification of the alcohol and tosylate as well as glpc separation of acetolysis products (see Experimental Section); the results, shown in eq 4, are



therefore tentative, but are analogous to those from VIIb. Figure 1 shows the partial nmr spectrum with tentative assignments indicated.

(19) R. S. Bly and R. T. Swindell, *J. Org. Chem.*, 30, 10 (1965).

Table VI. Estimated k_Δ Values for β-Allenic Ester Solvolyses at 65°

Compd	Model compound	k_s[a]	k_Δ[b]	$k_{\Delta,rel}$	k_Δ/k_s	$k_\Delta/k_{s,rel}$
IIb	*n*-Pentyl tosylate	3.73×10^{-7}	3.37×10^{-7}	1.00	0.90	1.00
IIIb	*n*-Hexyl tosylate	5.09×10^{-7}	1.08×10^{-6}	3.20	2.12	2.36
IVb	*n*-Heptyl tosylate	3.84×10^{-7}	1.19×10^{-6}	3.54	3.10	3.44
Ib	2-Hexyl tosylate	2.36×10^{-5}	4.4×10^{-6} [c]	13	0.19	0.20
d	2,2-Dimethylpentyl brosylate	1.88×10^{-7} [e]	3.09×10^{-4}	270[f]	1640	1820
Vc	2,2-Dimethylhexyl brosylate	1.93×10^{-7} [e]	9.93×10^{-4}	866[f]	5150	5720
VIe[g]	2-Methyl-2-butyl 3,5-dinitrobenzoate	3.62×10^{-6}	0[h]	0[h]	0[h]	0[h]
VIIb	*n*-Pentyl tosylate	3.73×10^{-7}	1.27×10^{-6}	3.77	3.40	3.78
VIIIb	*trans*-4-*t*-Butylcyclohexyl tosylate	1.01×10^{-5}	4.0×10^{-6}	12	0.40	0.44

[a] Estimated as the acetolysis rate of the model compound, Table III. [b] $k_\Delta = k_{t(allene)} - k_{t(model)}$. [c] Using the corrected value for k_t, see Table I. [d] 2,2-Dimethyl-3,4-pentadien-1-yl brosylate. Extrapolated from data in ref 7. [e] Extrapolated from the data in footnote *c*, Table III. [f] For ROTs, using $k_{Bros}/k_{Tos} = 3.40$. [g] For hydrolysis in 65% aqueous dioxane. [h] See text.

Discussion

The SN1 mechanism is now believed to proceed *via* ion pairs,[20] formation of which is the rate-determining step. The inherent assumption in interpretation of the results is that the observed titrimetric rate constant (k_t) directly reflects the rate of bond heterolysis when allowances are made for direct displacement by solvent (k_D).

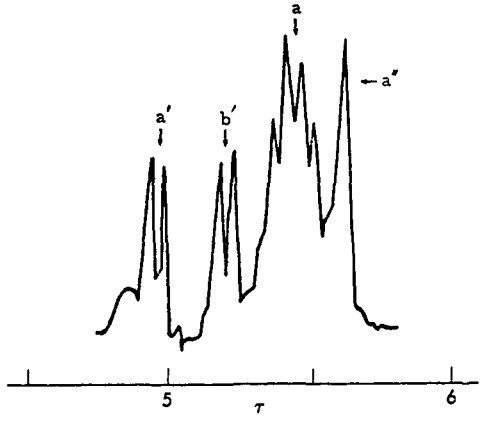


Figure 1. Partial 60-Mcps nmr spectrum of product mixture from acetolysis of VIIIb.

The specific rate for ion-pair formation is the sum of the unassisted (k_s) and assisted (k_Δ) specific rates. It is believed that relief of steric strain on going from ground state to transition state[21] will be small in the compounds studied. If bridging is important in the transition state it follows from Hammond's postulate[22] that the first-formed intermediate will also possess geometry-favoring delocalization.

In examination of kinetic data, simple comparison of titrimetric rate constants is often misleading because $k_t = k_s + k_D + k_\Delta$. To estimate k_Δ, model compounds were studied and the usual assumption was made that $k_{t(model)} = k_{s(model)} + k_{D(model)} = k_{s(allene)} + k_{D(allene)}$. Table VI gives the model compound used for each allene studied, $k_{t(model)}$, $k_{\Delta(allene)}$ (estimated as $k_{t(allene)} - k_{t(model)}$), and associated parameters.

Judging from the work of Bly,[7] the k_s terms for the allenic sulfonates are probably *less* than those of the saturated models, owing to the rate-retarding inductive effect of the allenyl moiety. Therefore the values of k_Δ and especially k_Δ/k_s should be taken as lower limits to the "true" values.

Additional support for the notion that a β-allenic group retards unassisted ionization is derived from the observation that hydrolysis of VIe is only one-third as fast as the saturated model compound.

Except for VIe, each compound examined showed a k_Δ of significant magnitude. Of these, unsubstituted 3,4-pentadien-1-yl tosylate (IIb) exhibited the smallest value, while the 2,2,5-trimethyl-substituted compound (Vb) had a k_Δ 866 times as great. The accelerative effects of substitution on the acetolysis k_Δ's for 3,4-pentadien-1-yl tosylates (at 65°) relative to the unsubstituted compound are summarized in Figure 2.

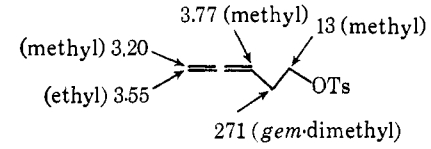


Figure 2. The effect of substitution on the k_Δ's of 3,4-pentadien-1-yl tosylates relative to the unsubstituted compound.

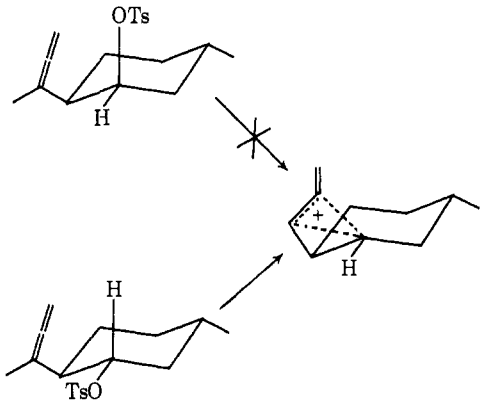
It is interesting that at least in the one instance where the additivity of the influence of methyl substitution on the k_Δ's can be checked with the compounds studied it comes out rather precisely. The ratio of k_Δ's for IIb and 2,2-dimethyl-3,4-pentadien-1-yl tosylate (Table VI) is 270; for Vb and IIIb the ratio is 271.

Methyl substitution at C_1 (the ionizing center) has several effects. First, rearrangement to a less reactive substrate occurs. Also, in comparison to IIb, k_Δ is 13 times as large, k_s is 65 times as great, and k_D has become much less important. As a result the ratio k_Δ/k_s is much smaller for Ib than for IIb, as would be expected on the basis of the fact that the more inherently stable (*i.e.*, due to classical effects) an incipient cationic center, the less it will rely on anchimeric assistance.[23] Since the absolute rate of rearrangement of Ib (1.35×10^{-5} sec^{-1}) exceeds k_Δ, it is apparent that either the $k_{s(model)}$ value is not an accurate measure of $k_{s(allene)}$, or, some leakage from classical ion to bridged ion is taking place.

Cyclic allenic tosylate VIIIb adds another dimension to this study. Although the configuration of the -OH

(20) S. Winstein, E. Clippinger, A. H. Fainberg, and G. C. Robinson, *J. Am. Chem. Soc.*, 76, 2597 (1954), and other papers in the series.
(21) H. C. Brown, *Chem. Eng. News*, 45, 86 (Feb 13, 1967).
(22) G. S. Hammond, *J. Am. Chem. Soc.*, 77, 334 (1955).
(23) S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *ibid.*, 74, 1113 (1952).

group could not be established unambiguously, it is believed, on the basis of the nmr spectrum and reactivity (*vide supra*), to be the equatorial epimer. Examination of molecular models suggests that participation by the allenic system is virtually impossible with the -OTs axial (provided the allenic moiety is equatorial). However, such assistance appears to be at least geometrically allowed when the tosylate group is equatorial as shown in eq 5. It is, in fact, found that VIIIb under-



(5)

goes acetolysis 50% faster than *trans*-4-*t*-butylcyclohexyl tosylate (diequatorial), with a k_Δ 12 times greater than IIb. The fact that k_Δ for VIIIb is about as great as that of Ib suggests that, although the allenyl moiety is confined to a conformation favorable for participation in the former case, ring strain counterbalances the effect by inhibiting formation of the bicyclic transition state for assisted carbonium ion production.

To summarize, the kinetic evidence strongly supports the hypothesis that homoallenic anchimeric assistance is favorably competitive with "simple" SN1 acetolyses in all cases studied except VIe.

It is significant that in every case where participation is kinetically inferred, rearranged products are formed and that the relative amount of rearranged or cyclized products varies directly with the relative magnitude of k_Δ (Table VII). This suggests that the unrearranged

Table VII. Correlation of k_Δ/k_s Ratio with Fraction of Cyclized or Rearranged Product

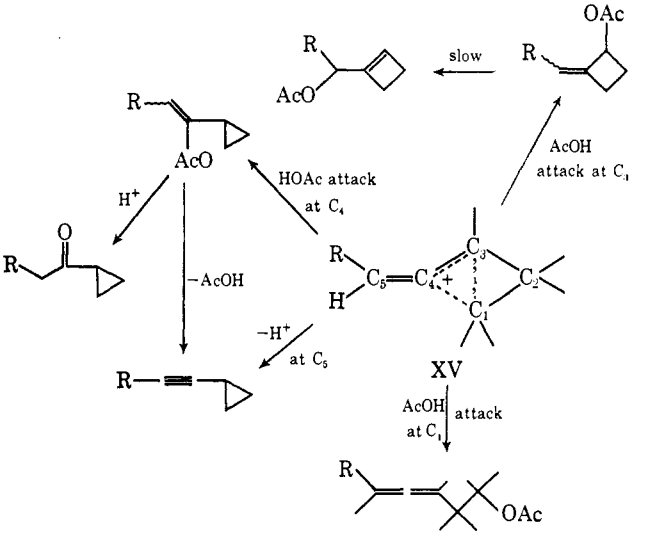
Compd	$k_\Delta/k_{s,rel}$ at 65°	% cyclized products (temp, °C)
VIe	0	0 (65)
VIIIb	0.44	50 (85)
Ib	0.50	35 (85)
IIb	1.00	24 (100)
IIIb	2.36	86 (85)
IVb	3.44	88 (85)
VIIb	3.78	89 (85)
Vb	5720	100 (65)

acetates arise mainly, if not exclusively, from classical ion intermediates (*via* the k_s route) while the cyclized and rearranged products arise specifically from bridged nonclassical intermediates.

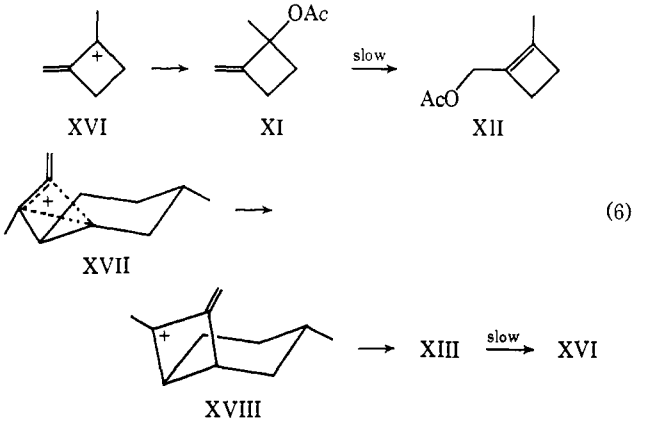
We have chosen to formulate the first-formed intermediate as a bicyclobutonium ion, XV (in which the predominance of positive charge resides at C_3 and C_4), in cases where homoallenyl participation is significant and have presented the discussion in terms of such ions. However, our work does not exclude formulation as a homoallyl cation, a cyclopropylcarbinyl cation, or some other ion. Interconversion of various bicyclobutonium ions[3] or of these with the other varieties of ions mentioned is easily envisaged. The problem was discussed recently[7] for homoallenyl compounds and will not be examined further here.

The observations that both optically active Ib and Vb yield optically active products require transition states and intermediates which retain their element of dissymmetry. Ion (or probably more precisely ion pair) XV is then trapped by solvent (as shown in Scheme I) unless a more stable classical ion is readily accessible.

Scheme I



In the case of VIIb, the first-formed ion related to XV probably opens rapidly to tertiary allylic cation XVI which is product determining (eq 6). Similarly, bicyclic carbonium ion XVII from VIIIb undergoes opening to XVIII, which is then trapped by solvent.



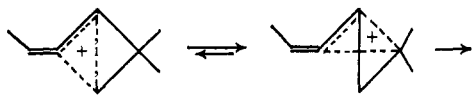
(6)

Slow rearrangement of methylene cyclobutanes to cyclobutenes, which is observed or implied in several of the product mixtures, is expected on the basis of the greater stability of the latter.[24]

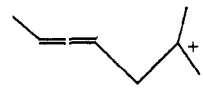
The first-formed intermediate from Vb and c, XIX, undergoes rapid equilibration to XX which then opens irreversibly to the more stable classical tertiary ion XXI, which is product determining (eq 7).

It is significant that throughout this work, no products arising from hydride or methyl migration were en-

(24) K. B. Wiberg and R. A. Fenoglio, *J. Am. Chem. Soc.*, 90, 3395 (1968).



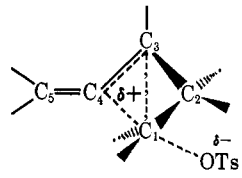
XIX XX



XXI (7)

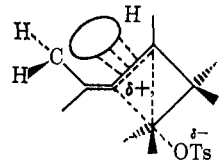
countered. This indicates that participation by the allenyl moiety leads to stabilized carbonium ions by way of a transition state lower in energy than one required for such migration.

If the first-formed intermediate is indeed XV, then Hammond's postulate requires that the best representation of the general transition state is the structure XXII.



XXII

The observed alkyl substitution effects can be qualitatively rationalized on the basis of this structure. Methyl substitution at either C_3 or C_1 has the expected effect of stabilizing the transition state through hyperconjugation and inductive interactions. *gem*-Dimethyl substitution at C_2 facilitates closure of the assisted transition state and is responsible for the largest rate enhancement observed in this study: a factor of 5000 over the saturated analog. The fact that a methyl group at C_5 is only slightly less effective than a 3-methyl group in enhancing the solvolytic rate is further evidence for some type of "homohyperconjugative" interaction as shown in XXIII. Such an effect has been previously suggested to explain the anomolous preference for terminal addition of 2,4-dinitrobenzenesulfenyl chloride to 2-methyl-2,3-butadiene.[25]



XXIII

Conclusion

On the basis of the evidence presented here, it is apparent that the allenyl system has the same versatility as the double bond for participation in the formation of β-carbonium ions. Although the question of which is more effective can only be resolved by additional work, it is clear that a β-allenyl moiety imparts a general enhancement of reactivity to systems undergoing solvolysis, except where the incipient cationic center is of sufficient inherent stability not to require assistance (*e.g.*, tertiary systems). As a result, k_Δ becomes competitive with k_s to an extent which ranges from k_Δ/k_s of 0.90 for IIb to over 5000 for Vb. We feel that this enhanced reactivity and the observation of rearranged and cyclized products in all cases (except VIe) are best explained on the basis of homoallenic participation in the rate-determining step of the solvolysis (illustrated by transition state XXII).

(25) T. L. Jacobs and R. Macomber, *J. Org. Chem.*, 33, 2988 (1968).

Experimental Section

Unless otherwise noted, analytical gas chromatography was carried out on a Perkin-Elmer Model 800 gas chromatograph (hydrogen flame ionization detector, nitrogen carrier gas), fitted with a 5 ft × 1/8 in. column containing 12% Dow Corning Silicone Oil 550 on 80–100 Chromosorb W. Product ratios were computed from analytical glpc peak areas, and are not corrected for differences in detector response. A Loenco Model 160 Prep-Matic (thermal conductivity detector, helium carrier gas), fitted with a 10 ft × 3/8 in. column packed with 20% D. C. Silicone Oil 550 on 30–60 Chromosorb W, was used for preparative separations. Glpc conditions 100/110-30 are to be interpreted: column temperature 100°; injection block temperature 110°; carrier gas flow rate 30 cc/min. Temperature programming is indicated by →150 at 10, meaning the column was heated from initial conditions to 150° at a rate of 10°/min. For components isolated by preparative glpc, *rt* = retention time (min); *ra* = relative abundance.

Melting points were measured on a Büchi oil bath apparatus in open capillary tubes; Anshutz thermometers were used. Distillations were performed with Vigreux columns; boiling points and corresponding pressures (Zimmerli gauge) are uncorrected. Optical rotations were measured on a Perkin-Elmer Model 141 polarimeter with digital readout, using 1.00-dm cells.

Ultraviolet spectra were run in 1.00-cm cells on a Cary Model 14 spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer Infracord 137, with 0.42-mm cells, in carbon tetrachloride solution; absorption values are given in units of cm^{-1}. Nmr spectra were taken at ambient temperature on a Varian A-60 (made available by funds from the National Science Foundation), with samples in carbon tetrachloride. Spectral values are reported as follows: τ 3.9 (d, J = 9 cps, 2 H), to be interpreted as τ, 3.9, doublet (s = singlet, t = triplet, q = quartet, m = multiplet), J = 9 cps, relative integration two protons (±5%). Chemical shift values refer either to internal (ntms) or external (xtms) tetramethylsilane (τ 10.0) as noted. All spectral assignments are in agreement with the expected values.

cis- and *trans*-**2-penten-4-yn-1-ol** were prepared in 10% yield by the method of Hanack and Haffner,[6] bp 62–65° (11.5 mm) [lit.[6] 65–66° (12 mm)]; ir: 3400 (broad, OH), 2130 (C≡C), 1650 (C=C); nmr (ntms): τ 3.55 (t), 3.8 (5), 4.1–4.6 (complex absorption), 5.5–6.0 (broad envelope), 6.8 (d, J = 2 cps), and 7.1 (d, J = 2 cps).

3,4-Pentadien-1-ol (IIa). Reaction of the mixture of *cis*- and *trans*-2-penten-4-yn-1-ols with an equimolar amount of lithium aluminum hydride according to the previously published procedure[6] afforded a 74% yield of 3,4-pentadienol, bp 52–53° (10.5 mm) [lit.[6] 48° (10 mm)]. Glpc (90/105-30) showed only one peak at 2.4 min; ir: 3400 (broad, OH) 1970 (C=C=C); nmr (ntms): τ 5.0 (q, J = 7 cps, 1 H), 5.37 (perturbed q, J = 3 cps, 2 H), 5.58 (s, 1 H), 6.43 (t, J = 7 cps, 2 H), and 7.8 (symmetrical m, 2 H).

Anal. Calcd for C_5H_8O: C, 71.39; H, 9.58. Found: C, 70.93; H, 9.53.

3,4-Pentadien-1-yl Tosylate (IIb). The *p*-toluenesulfonates and *p*-bromobenzenesulfonates used in this study were prepared similarly. Below is the typical procedure. To a cold (0°) solution of 5.25 g (27.5 mmol) of *p*-toluenesulfonyl chloride in 20 ml of dry pyridine was added 2.10 g (25.0 mmol) of 3,4-pentadien-1-ol. After gentle swirling, the solution was allowed to stand at −20° for 24 hr. (More hindered alcohols required up to 48 hr.) The resulting solution containing crystals of pyridine hydrochloride was poured onto 25 g of an ice–water slurry. The suspension was stirred until the ice had melted, then extracted with a total of 25 ml of ether. The ether solution was washed with 1 *N* hydrochloric acid (to pH 1), 5% sodium bicarbonate, and saturated sodium chloride, then dried at 0° over molecular sieves. Removal of solvent at the rotary evaporator, then evacuation at 0.2 mm for 1 hr left 5.5 g (93%) of the tosylate as a clear colorless oil; ir: (no OH), 1975 (C=C=C), 1610 (aromatic C=C), and 1380 ($-SO_2-$); nmr (ntms): τ 2.27 (perturbed d, J = 7 cps, 2 H), 2.70 (perturbed d, J = 7 cps, 2 H), 5.0 (q, 1 H), 5.3 (m, 2 H), 5.99 (t, J = 6.5 cps, 2 H), 7.60 (s, 3 H), and 7.7 (symmetric m, 2 H).

Anal. Calcd for $C_{12}H_{14}O_3S$: C, 60.50; H, 5.92. Found: C, 60.73; H, 5.86.

3,4-Pentadien-1-yl brosylate (IIc) had an 83% yield as a clear colorless oil; ir: (no OH), 3120 (=CH_2), 1980 (C=C=C), 1590 (aromatic

C=C), and 1380 (-SO_2-); nmr (ntms): τ 2.30 (s, 4 H), 5.0 (m, 1 H), 5.3 (m, 2 H), 5.92 (t, J = 7 cps, 2 H), and 7.67 (symmetrical m, 2 H).

Anal. Calcd for $C_{11}H_{11}BrO_3S$: C, 43.57; H, 3.66. Found: C, 43.82; H, 3.55

3,4-Pentadien-1-yl Acetate (IId). The following is typical of the procedure for preparation of authentic acetate esters. A solution of 8.4 g (10 mmol) of 3,4-pentadien-1-ol and 1.12 g (11 mmol) of acetic anhydride in 8 ml of pyridine was heated over steam for 4 hr (more hindered alcohols require up to 10 hr). The solution was cooled and poured onto 15 g of an ice–water slurry, which was then extracted with a total of 15 ml of ether. The ether solution was washed and dried as in the preparation of the sulfonate esters. Removal of solvent and bulb-to-bulb distillation afforded 1.0 g (80%) of a sweet smelling liquid, bp 70° (15 mm); ir: (no OH), 1980 (C=C=C), and 1755 (C=O); nmr (ntms): τ 5.0 (q, 1 H), 5.3 (m, 2 H), 5.95 (t, J = 6.5 cps, 2 H), 7.7 (symmetric m, 2 H), and 8.03 (s, 3 H).

Anal. Calcd for $C_7H_{10}O_2$: C, 66.64; H, 7.99. Found: C, 66.60; H, 8.23.

Acetolysis of IIb. A solution of 13.0 g (0.055 mol) of the tosylate in 300 ml of preparative acetolysis solvent (*vide infra*) was heated to 100.0° in an oil bath for 56 hr (*ca.* seven half-lives). The mixture was cooled to ambient temperature, diluted with an equal volume of water, then extracted with a total of 75 ml of petroleum ether (bp 20–40°). This solution was washed twice with 5% sodium bicarbonate and once with water, then dried at 0° over sieves. The dry solution was subjected to analytical glpc to obtain product ratios, then ~75% of the solvent was allowed to evaporate. The resulting concentrate was separated into its components by preparative glpc, then each isolated component was resubjected to analytical glpc to assign the correct peaks and to test for stability under the separation conditions. Preparative glpc (100/145-180 for 9 min; then →140 at 5) yielded the following compounds.

First component: *rt* 7.3; *ra* 11%; ir: 3020 (cyclopropyl CH), 1710 (C=O), and 1030 (cyclopropyl CH_2); nmr (xtms): τ 7.90 (s, 3 H, H_b), 8.1 (m, 1 H, H_c), 9.2 (complex m, 4 H, H_a); assignment: cyclopropyl methyl ketone.

Second component: *rt* 10.8; *ra* 4%; ir: 3000–2800 (aliphatic and allenic CH), 1960 (C=C=C), 1720 (?, less intense than absorption at 1960; not due to an impurity), 1440, and 1290; nmr (xtms): τ 4.95 (perturbed q, 1 H), 5.3 (m, 2 H), 6.52 (t, J = 7 cps, 2 H), and 7.6 (broad envelope, 2 H). Although the nmr spectrum is very similar to that of IIa, there is no OH absorption in the ir spectrum. The tentative structure assignment is di(3,4-pentadien-1-yl) ether.

Third and fourth components (these fractions were collected together—although analytical glpc definitely showed two components, they could not be resolved on the preparative instrument): *rt* 15.2; *ra* 9%. The mixture could not be isolated free enough from IId to allow meaningful spectra to be obtained. By their retention times they are undoubtedly acetates, and by analogy with the products from the acetolyses of 3,4-hexadienyl and 3,4-heptadienyl tosylates (*vide infra*) these compounds are most likely 2-methylenecyclobutyl acetate and 1-cyclopropyl-1-acetoxyethylene.

Anal. Calcd for $C_7H_{10}O_2$: C, 66.64; H, 7.99. Found: C, 66.24; H, 8.17.

Fifth component: *rt* 22.1; *ra* 76%. This compound was identical in all respects with authentic IId.

Anal. Calcd for $C_7H_{10}O_2$: C, 66.64; H, 7.99. Found: C, 66.50; H, 8.36.

Test for Return of IIb. A solution of 1.5 g of tosylate IIb in 25 ml of dry acetic acid containing 0.8 g of sodium acetate was heated to 100° for 12 hr (~1.5 half-lives), then cooled and worked up as with the preparative acetolyses. Removal of solvent followed by vacuum removal of most of the volatile material at 0.2 mm left 0.2 g of pale yellow oil. The nmr spectrum showed only unrearranged IIb, contaminated with a small amount of unrearranged acetate IId.

2-Hexen-4-yn-1-ol. Reaction of sodium propynide with epichlorohydrin in a manner exactly analogous to the preparation of 2-penten-4-yn-1-ol gave a 45% yield of *cis*- and *trans*-2-hexen-4-yn-1-ols, bp 63–77° (2.9 mm) [lit.[6] 83–84° (7 mm)]. Glpc (125/145-30) showed peaks at 2.8 min (40%) and 4.0 min (60%); ir: 3400 (broad, OH), 2250 (C≡C), and 1650 (C=C); nmr (xtms): τ 3.5–4.6 (complex absorption), 5.6–6.0 (broad envelope), and 8.0 (two superimposed doublets); uv (methanol): λ_{max} 223 (log ϵ 4.02) and 231 mμ (log ϵ 3.95).

3,4-Hexadien-1-ol (IIIa). Treatment of 2-hexen-4-yn-1-ol with an equimolar amount of lithium aluminum hydride (reflux time 5.5 hr) afforded a 94% yield of 3,4-hexadienol contaminated with ~10% of an isomeric conjugated diene. Distillation through a Nester–Faust spinning-band column gave IIIa, bp 63–66° (9 mm) [lit.[6] 64–65° (10 mm)], which was >98% pure by glpc (*rt* 2.2 at 125/145-30); ir (neat): 3400 (broad, OH), 1975 (C=C=C); pmr (ntms): τ 5.0 (m, 2 H), 5.58 (s, 1 H), 6.45 (perturbed t, J = 7 cps, 2 H), 7.85 (symmetrical m, 2 H), and 8.4 (perturbed d of doublets, 3 H).

Anal. Calcd for $C_6H_{10}O$: C, 73.42; H, 10.27. Found: C, 72.21; H, 10.43.

3,4-Hexadien-1-yl tosylate (IIIb) was a clear, colorless oil prepared in 85% yield; ir: (no OH), 1975 (C=C=C), 1610 (aromatic C=C), 1370 (-SO_2-); nmr (xtms): τ 2.34 (perturbed d, J = 8 cps, 2 H), 2.77 (perturbed d, J = 8 cps, 2 H), 5.1 (m, 2 H), 6.08 (t, J = 7 cps, 2 H), 7.67 (s, 3 H), and 7.8 (m, 2 H), 8.51 (d of doublets, 3 H).

Anal. Calcd for $C_{13}H_{16}O_3S$: C, 61.89; H, 6.39. Found: C, 62.01; H, 6.42.

3,4-Hexadien-1-yl brosylate (IIIc) was prepared in 75% yield; ir: (no OH), 1980 (C=C=C), 1580 (aromatic C=C), and 1380 (-SO_2-); nmr (xtms): τ 2.30 (s, 4 H), 5.05 (m, 2 H), 5.93 (t, J = 6.5 cps, 2 H), 7.7 (m, 2 H), and 8.42 (d of doublets, 3 H).

Anal. Calcd for $C_{12}H_{13}BrO_3S$: C, 45.44; H, 4.13. Found: C, 45.96; H, 4.42.

3,4-Hexadien-1-yl Acetate (IIId). Ester IIId was prepared in 80% yield; ir: (no OH), 1980 (C=C=C), and 1755 (C=O); nmr (xtms): τ 5.2 (m, 2 H), 6.16 (t, J = 7 cps, 2 H), 7.9 (m, 2H), 8.25 (s, 3 H), and 8.59 (d of doublets, 3 H).

Anal. Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.45; H, 8.60.

Acetolysis of IIIb. A solution of 10.5 g (42 mmol) of IIIb in 250 ml of preparative acetolysis solvent was heated to 85° for 6 days (*ca.* ten half-lives). The solution was cooled and worked up as in the acetolysis of IIb, and the components were separated by preparative glpc (135/170-180).

First Component: *rt* 5.0; *ra* 31%; ir: 3110, 3020 (cyclopropyl CH), 2150 (C≡C), 1725 (C=O from second component as impurity), and 1040 (cyclopropyl CH_2); nmr (xtms): τ 8.02 (sharp m, 1 H); 8.39 (d, J = 2 cps, 3 H), and 9.5 (m, 4 H); assignment: cyclopropylmethylacetylene.

Second Component: *rt* 11.5; *ra* 5%; ir: 3020 (cyclopropyl CH), and 1710 (C=O); nmr (xtms): τ 7.54 (q, J = 7 cps, 2 H), 8.15 (m, 1 H), 9.11 (t, J = 7 cps, 3 H), and 9.3 (m, 2 H); melting point of 2,4-DNPH 154–156° dec; assignment: cyclopropyl ethyl ketone.

Anal. Calcd for $C_6H_{10}O$: C, 73.43; H, 10.27. Found: C, 70.22; H, 10.29.[26]

Third component: *rt* 25; *ra* 7%; ir: 1755 (ester C=O), 1650 (weak C=C), and 850 (trisubstituted double bond); nmr (xtms): τ 4.26 (broad s, 1 H), 4.9 (m, 1 H), 7.8 (m, 4 H), 8.11 (s, 3 H), 8.80 (d, J = 6 cps, 3 H); assignment: 1-cyclobutenylethyl acetate.

Fourth and fifth components (collected together): *rt* 31 and 33; *ra* 7 and 8%, respectively; ir: 3100 (shoulder, cyclopropyl CH), 1760 and 1750 (C=O), and 845 (trisubstituted double bond); nmr (xtms): τ 4.4–5.3 (complex absorption), 7.7 (m), 8.05 and 8.14 (singlets), 8.55 (d of doublets), 8.70 (d, J = 7 cps), and 9.6 (m); assignment: the mixture contains *syn*- (on the basis of the lower field methyl absorption, *vide infra*) 2-ethylidenecyclobutyl acetate and *cis*- or *trans*-1-cyclopropylpropenyl acetate.

Anal. Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 67.07, H, 8.78.[26]

Sixth component: *rt* 38; *ra* 27%; ir: 1755 (C=O) (this spectrum is very similar to that of the preceding mixture); nmr (xtms): τ 4.7 (m, 2 H), 7.6–8.3 (m, 4 H), 8.18 (s, 3 H), and 8.63 (d of doublets, 3 H); assignment: because of the slightly higher chemical shift of the olefinic methyl group (8.63 *vs.* 8.55) and because of steric preference for this isomer by a ratio of 4:1, this component is most likely *anti*-2-ethylidenecyclobutyl acetate.

Anal. Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 67.67; H, 8.77.[26]

Seventh component: *rt* 43; *ra* 14%. The spectra of this compound were identical with those of authentic IIId.

Anal. Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63; Found: C, 67.18; H, 8.82.[26]

2-Hepten-4-yn-1-ol. The reaction of epichlorohydrin with the sodium salt of butyne in liquid ammonia in a manner analogous to

(26) Several of the acetolysis products isolated by glpc gave elemental analyses in which the value for carbon was low and the hydrogen high. This is believed due to the presence in the carrier gas of water which could not be successfully removed. Similar problems were encountered by Bly.[19]

the preparation of 2-penten-4-yn-1-ol afforded a 15% yield of *cis*- and *trans*-2-hepten-4-yn-1-ols, bp 73–77° (3 mm). Analytical glpc (125/145-30) showed peaks at 4.1 min (45%) and 6.5 min (55%); ir: 3400 (broad OH), 2240 (C≡C), and 1650–1630 (C=C); nmr (ntms): τ 3.7–4.7 (complex absorption, 2 H), 5.6 and 5.9 (doublets, 2 H), 5.8 (broad s, 1 H), 7.75 (m, 2 H), and 8.85 (t, J = 8 cps, 3 H); uv (methanol): λ_{max} 227 (log ϵ 4.17) and 235 mμ (log ϵ 4.10).

3,4-Heptadien-1-ol (IVa). In a manner exactly similar to the preparation of IIa, 2-hepten-4-yn-1-ol was refluxed with an equimolar amount of lithium aluminum hydride for 6 hr, then worked up as usual. As with IIIa, the product was contaminated with ~15% conjugated diene isomers, which were removed through careful distillation with a spinning-band column yielding 75% of alcohol IVa, bp 67–68° (9.5 mm). Analytical glpc(115 /140-30) showed a peak at 3.8 min representing >99% of the sample; ir: 3400 (broad OH), 1975 (C=C=C), and 1050 (CO); nmr (ntms): τ 4.9 (quintet, J = 5 cps, 2 H), 5.52 (s, 1 H), 6.4 (perturbed t, J = 7 cps, 2 H), 7.6–8.3 (m, 4 H), and 9.0 (perturbed t, J = 7, 3 H).

Anal. Calcd for $C_7H_{12}O$: C, 74.95; H, 10.78. Found: C, 74.85; H, 10.70.

3,4-Heptadien-1-yl Tosylate (IVb). The usual method resulted in an 87% yield; ir: (no OH), 1980 (C=C=C), 1610 (aromatic C=C), 1370 (-SO_2-); nmr (xtms): τ 2.33 (perturbed d, J = 8 cps, 2 H), 2.77 (perturbed d, J = 8 cps, 2 H), 5.0 (m, 2 H), 6.05 (perturbed t, J = 7 cps, 2 H), 7.65 (s, 3 H), 7.6–8.4 (m, 4 H), and 9.11 (perturbed t, J = 7 cps, 3 H).

Anal. Calcd for $C_{14}H_{18}O_3S$: C, 63.14; H, 6.81. Found: C, 63.29; H, 6.89.

3,4-Heptadien-1-yl brosylate (IVc) was prepared in 75% yield; ir: (no OH), 1980 (C=C=C), 1590 (aromatic C=C), and 1390 (d, -SO_2-); nmr (xtms): τ 2.31 (s, 4 H), 5.0 (m, 2 H), 5.97 (t, J = 6.5 cps, 2 H), 7.5–8.3 (m, 4 H), and 9.08 (t, J = 7 cps, 3 H).

Anal. Calcd for $C_{13}H_{15}BrO_3S$: C, 47.15; H, 4.57. Found: C, 47.25; H, 4.65.

3,4-Heptadien-1-yl acetate (IVd) was prepared in quantitative yield by refluxing the corresponding alcohol in acetic anhydride for 10 hr; ir: (no OH), 1980 (C=C=C), 1760 (ester C=O); nmr (xtms): τ 5.1 (m, 2 H), 6.12 (t, J = 7 cps, 2 H), 7.7–8.4 (m) and 8.21 (s) totaling 7 H, and 9.18 (t, J = 7 cps, 3 H).

Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.52; H, 9.85.

Acetolysis of IVb. A solution of 11.6 g (44 mmol) of IVb in 250 ml of preparative acetolysis solvent was heated to 85° for 5 days (*ca.* nine half-lives) then cooled and worked up as usual. The product mixture was separated *via* preparative glpc (135/170-180).

First component: *rt* 5.5; *ra* 1%; not identified.

Second component: *rt* 7.5; *ra* 27%; mass spectrum (MS-9, 70 eV): parent peak at 94 (C_7H_{10}); ir: 3120 and 3030 (cyclopropyl CH), 2250 (C≡C), and 1725 (weak C=O due to third component as impurity); nmr (xtms): τ 8.0 (perturbed q of doublets, J = 7 cps, 2 H) and (m) totaling 3 H, 9.01 (perturbed t, J = 7 cps, 3 H), and 9.4 and 9.5 (sharp multiplets) totaling 4 H; assignment: cyclopropylethylacetylene.

Anal. Calcd for C_7H_{10}: C, 89.30; H, 10.70. Found: C, 84.63; H, 10.40.[26]

Third component: *rt* 15; *ra* 16%; ir: 3100 and 3020 (cyclopropyl CH), 1700 (C=O), and 1030 (cyclopropyl CH_2); nmr (xtms): τ 7.60 (perturbed t, J = 7 cps, 2 H), 8.08–8.8 (complex absorption, 3 H), and 9.25 (m, 7 H); melting point of 2,4-DNPH 153–154°; assignment: cyclopropyl propyl ketone.

Anal. Calcd for $C_7H_{12}O$: C, 74.95; H, 10.78. Found: C, 73.72; H, 10.70.[26]

Fourth component: *rt* 23; *ra* 4%; ir: 1970 (C=C=C), 1720 and 1750 (C=C, not intense enough to be C=O); tentative assignment: 1,3,5-heptatriene.

Fifth component: *rt* 33; *ra* 4%; ir: 1755 (ester C=O) and 865 (trisubstituted C=C); nmr (xtms): τ 4.2 (sharp m, 1 H), 5.0 (m, 1 H), 7.65 [sharp m, 3 H (theoretical 4 H)], 8.05 (s, 3 H), 8.5 (q of doublets, J = 7 cps, 1, 2 H), 9.17 (t, J = 7 cps, 3 H); assignment: 1-cyclobutenylpropyl acetate.

Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 69.02; H, 8.66.[26]

Sixth and seventh components (collected together): *rt* 37 and 40; *ra* 4 and 9%, respectively; ir: 1755 (broad, ester C=O) and 870 (trisubstituted double bond); nmr (xtms): τ 5.2–6.3 (complex absorption), 7.5–7.9 (m), 8.00 and 8.09 (singlets), 8.1–8.4 (m), 9.1 (two superimposed triplets, $J \cong 7$ cps), and 9.55 (m); assignment: by analogy with the results from IIIb, the sixth component is *cis*- and/or *trans*-1-cyclopropyl-1-butenyl acetate, and the seventh is *syn*-2-propylidenecyclobutyl acetate.

Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 69.88; H, 9.28.

Eighth component: *rt* 48; *ra* 16%; ir: (very similar to that of the above mixture) 1765 (C=O) and 865 (trisubstituted C=C); nmr (xtms): τ 4.5–5.0 (envelope, 2 H), 7.6–8.4 (multiplets) and 8.13 (s) totaling 9 H, and 9.15 (t, J = 7 cps, 3 H); assignment: *anti*-2-propylidenecyclobutyl acetate.

Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 69.83; H, 9.36.

Ninth component: *rt* 58; *ra* 12%. The spectral properties of this component were the same as those of authentic IVd.

Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 69.93; H, 9.05.

Tenth component: *rt* 70; *ra* 5%; ir: 2250 (very weak, C≡C) and 1760 (ester C=O); nmr (xtms): τ 5.95 (t, J = 6.5, 2 H); 7.6–8.0 (m, 4 H), 8.07 (s, 3 H), 8.1–8.5 (m, 2 H), 8.96 (t, J = 7 cps, 3 H); assignment: 4-heptynyl acetate. This isomer was chosen instead of 3-heptynyl acetate owing to the absence of absorption at τ 8.7.

Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.04; H, 9.11.

Test for Return of IVb. A solution of 3.0 g of IVb in 50 ml of dry acetic acid containing 20 mmol of anhydrous sodium acetate was heated to 85° for 20 hr (~1.5 half-lives). The solution was cooled, then extracted as in the preparative acetolyses. The petroleum ether solution was evaporated and the residue subjected to evacuation at 0.2 mm for 3 hr to remove all volatile material. A nmr spectrum of the resulting oil was identical with that of unrearranged IVb. A small amount of IVd was also observed.

4,5-Hexadien-2-ol (Ia)[4] was obtained in 95% yield through the lithium aluminum hydride reduction of 3-hexen-1-yn-5-ol,[27] which, in turn, was produced through acid-catalyzed rearrangement of *trans*-4-hexen-1-yn-3-ol.[28] The spectral data for Ia were as follows: ir: 3400 (broad, OH) and 1975 (C=C=C); nmr (ntms): τ 4.9 (q of doublets, J = 7 and 2 cps, 1 H), 5.4 (m, 2 H), 5.83 (broad s, 1 H), 6.2 (q, J = 7 cps, 1 H), 7.9 (m, 2 H), 8.83 (d, J = 6 cps, 3 H).

Anal. Calcd for $C_6H_{10}O$: C, 73.43; H, 10.27. Found: C, 73.22; H, 10.35.

4,5-Hexadien-2-yl tosylate (Ib) was prepared in 83% yield; ir: (no OH), 3020 (=CH_2), 1960 (C=C=C), 1610 (aromatic C=C), and 1380 (-SO_2-); nmr (ntms): τ 2.27 (perturbed d, J = 8 cps, 2 H), 2.70 (perturbed d, J = 8 cps, 2 H), 5.2 (perturbed q of doublets, J = 8 and 2 cps, 1 H), 5.4 (m, 3 H), 7.63 (s, 3 H), 7.8 (m, 2 H), and 8.76 (d, J = 6 cps, 3 H).

Anal. Calcd for $C_{13}H_{16}O_3S$: C, 61.89; H, 6.39. Found: C, 62.01; H, 6.52.

4,5-Hexadien-2-yl brosylate (Ic) was prepared in 75% yield and showed the following spectral data; ir: (no OH), 3030 (=CH_2), 1970 (C=C=C), 1590 (aromatic C=C), and 1380 (-SO_2-); nmr (ntms): τ 2.30 (s, 4 H, this band had very slight fine structure), 4.9–5.6 (m, 4 H), 7.7 (m, 2 H), and 8.68 (d, J = 6 cps, 3 H).

Anal. Calcd for $C_{12}H_{13}BrO_3S$: C, 45.44; H, 4.13. Found: C, 45.80; H, 4.34.

4,5-Hexadien-2-yl acetate (Id) was prepared in 80% yield; ir: (no OH), 1980 (C=C=C), and 1770 (ester C=O); nmr (ntms): τ 4.8–5.5 (two multiplets, 4 H), 7.8 (m, 2 H), 8.05 (s, 3 H), and 8.89 (d, J = 6 cps, 3 H).

Anal. Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.28; H, 8.75.

Acetolysis of Ib. A solution of 22.7 g (90 mmol) of Ib in 250 ml of dry acetic acid containing 100 mmol of anhydrous sodium acetate was heated to 85° for 27 hr (*ca.* ten half-lives). Work-up as usual, followed by preparative glpc (110 → 150 at 2/158-180) afforded the following components.

First component: *rt* 10.6; *ra* 22%; ir: 3000 (cyclopropyl CH) and 1705 (C=O); nmr (xtms): τ 7.90 and 7.93 (singlets of essentially equal intensity), 7.8–8.3 (m), and 8.8–9.2 (complex absorption); melting point of 2,4-DNPH 115–118° (lit.[4] 122°); assignment: *cis*- and *trans*-2-methylcyclopropyl methyl ketones.

Anal. Calcd for $C_6H_{10}O$: C, 73.43; H, 10.27. Found: C, 70.63; H, 10.27.[26]

Second and third components (collected together): *rt* 19–20; *ra* 8 and 3%, respectively; ir: 3100 (=CH_2), 1760 (ester C=O), 1690 (C=C, strained), and 890 (disubstituted C=C); nmr (xtms):

(27) E. B. Bates, E. R. H. Jones, and M. C. Whiting, *J. Chem. Soc.*, 1854 (1954).

(28) I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *ibid.*, 81 (1945); E. R. H. Jones, L. Skattebol, and M. C. Whiting, *ibid.*, 4765 (1956).

τ 5.5–5.8 (envelope, 3 H), 7.3 (envelope, 1 H), 7.8–8.3 (envelope), 8.14 and 8.15 (singlets) totaling 5 H, 8.91 and 8.93 (doublets, J = 6 cps, 3 H); assignment: *cis*- and *trans*-3-methyl-2-methylenecyclobutyl acetates.

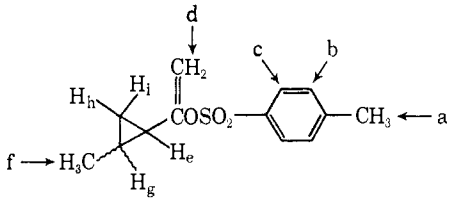
Anal. Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 67.19; H, 8.65.[26]

Fourth component: *rt* 23; *ra* 2%; not identified, but most likely an ester judging from retention time.

Fifth component: *rt* 25; *ra* 65%. This compound was identical in all respects with authentic Id.

Anal. Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.51; H, 8.65.

Test for Return of Ib. A sample (2.3 g) of Ib was dissolved in 50 ml of dry acetic acid containing 15 mmol of sodium acetate, and the resulting solution was heated to 85° for 3.8 hr (*ca.* two half-lives). The unreacted tosylate was extracted into ether following the same procedure as for the isolation of acetolysis products. Removal of solvent and volatile products at 0.2 mm left an oil, the nmr spectrum of which showed (ntms): τ 2.23 (perturbed d, J = 7 cps, 2 H, H_c), 2.67 (perturbed d, J = 7 cps, 2 H, H_b), 5.1–5.5 (m, 2 H, H_d), 7.60 (s, 3 H, H_a), 7.6–8.2 (envelope, 1 H, H_e), 8.75 (m containing doublet, 3 H, H_f), and 9.03 (sharp m, H_g, H_h, and H_i). Comparison of this spectrum with that of the unrearranged starting material shows that essentially quantitative rearrangement has taken place to give *cis*- and/or *trans*-(2-methylcyclopropyl)-1-ethenyl tosylate.



In order to ascertain the rate of disappearance of Ib at 65°, 5.2 g of the allenic tosylate was dissolved in 100 ml of preparative acetolysis solvent, then heated to 65.0°. At the intervals listed in Table VIII 25-ml aliquots were withdrawn and worked up as before.

Table VIII. The Total Rate of Disappearance of Ib

Time, 10^4 sec	I_Δ/I_{CH_3}	[Acid], M	[RT],[a] M	[Ib], M	Ln ([Ib]$_0$/[Ib])
0.0	0.0	0.0	0.0	0.206	0
3.0	0.436	0.0634	0.0624	0.081	0.83
5.9	0.694	0.103	0.712	0.032	1.64

[a] Ratio of the cyclopropyl proton integration to the tosyl methyl integration. This ratio is identical with the ratio [RT]/([RT] + [Ib]), where [RT] is the concentration of rearranged tosylate. Similarly ([RT] + [Ib]) is identical, by mass balance, to ([Ib]$_0$ − [acid]), the first term being the initial substrate concentration, the second being the concentration of liberated *p*-toluenesulfonic acid found by titration.

The nmr spectrum of each sample was run and the series showed the following trends: the absorptions for the protons (aromatic and methyl) remained constant in position and intensity; the allenic proton absorption became very complex with the lower region disappearing completely; the multiplet at τ ~7.8 decreased with time; the allenic methyl doublet decreased rapidly, being replaced by an unstructured multiplet containing a new doublet; finally, a new sharp multiplet with a broad base (due to H_g, H_h, and H_i in the above structure) appeared and increased rapidly in intensity. The integration of this latter absorption was well enough resolved from others that it was possible to compare its intensity with that of the tosyl methyl group. The ratio of the values approached 1.0 with time, confirming the assignment. Table VIII lists the integration values and derived concentration ratios *vs.* time. A least-squares treatment of the data gives a first-order rate constant for the disappearance of Ib, 2.8×10^{-5} sec^{-1}. The $k_r = (k_{disappearance} - k_{titrimetric})$ has the value 1.35×10^{-5} sec^{-1}.

2,2-Dimethyl-3,4-hexadien-1-ol (Va) had the following properties: ir: 3500 (broad, OH) and 1970 (C=C=C); nmr (neat, ntms): τ 4.9 (m, 2 H), 5.70 (s, 1 H), 6.70 (s, 2 H), 8.4 (d of doublets, 3 H), and 9.01 (s, 6 H). Analytical glpc (86/121-30) showed a single peak at 5.4 min.

Partial Resolution of Va. The allenic alcohol was partially resolved by fractional crystallization of the brucine salt of the phthalate half-ester.[9] Decomposition of the concentrated solutions of the more soluble diastereoisomer afforded Va, $[\alpha]^{25}D$ −6.6° (*c* 6, ethanol). The spectra and chemical properties of the active and racemic alcohols were identical.

2,2-Dimethyl-3,4-hexadien-1-yl tosylate (Vb), a clear colorless oil, was prepared in 86% yield; ir: (no OH), 1980 (C=C=C), 1610 (aromatic C=C), and 1380 (−SO_2−); nmr (ntms): τ 2.25 (perturbed d, J = 8 cps, 2 H), 2.70 (perturbed d, J = 8 cps, 2 H), 5.0 (m, 2 H), 6.33 (s, 2 H), 7.57 (s, 3 H), 8.4 (d of doublets, 3 H), and 9.01 (s, 6 H).

Anal. Calcd for $C_{15}H_{20}O_3S$: C, 64.26; H, 7.19. Found: C, 64.40; H, 7.18.

2,2-Dimethyl-3,4-hexadien-1-yl brosylate (Vc), a slightly cloudy oil, was prepared in 97% yield. The oil could be crystallized by redissolving it in a minimum amount of boiling petroleum ether, then allowing the solution to stand at −20°. Obtained in this way, the brosylate has mp 30.2–30.6°. When active Va was employed, the resulting ester had $[\alpha]^{25}D$ −2.67° (*c* 8, carbon tetrachloride); ir: (no OH), 1980 (C=C=C), 1590 (aromatic C=C), and 1380 (−SO_2−); nmr (ntms): τ 2.23 (s, 4 H), 5.0 (m, 2 H), 6.23 (s, 2 H), 8.4 (d of doublets, 3 H), and 9.00 (s, 6 H).

Anal. Calcd for $C_{14}H_{17}BrO_3S$: C, 48.70; H, 4.96. Found: C, 48.93; H, 5.09.

2,2-Dimethyl-3,4-heptadien-1-yl acetate (Vd) was prepared in 80% yield, bp ~90° (15 mm); ir: (no OH), 1960 (C=C=C), 1750 (ester C=O), and 1370 (acetate); nmr (ntms): τ 4.9 (m, 2 H), 6.18 (s, 2 H), 8.00 (s, 3 H), 8.3 (d of doublets, 3 H), 8.97 (s, 6 H). Analytical glpc (85/175-30 for 9 min, then →135 at 16) showed only one peak at 13.7 min.

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.58. Found: C, 71.11; H, 9.44.

Acetolysis of Vb. The tosylate (25 g, 90 mmol) was dissolved in 500 ml of preparative acetolysis solvent and the solution was heated to 65° for 8 hr (11 half-lives). The solution was cooled and products isolated as usual. Preparative glpc conditions were 110 → 155 at 6/160-300.

First component: *rt* 5.9; *ra* (*vide infra*); ir: 3090 (=CH_2), 1980 (C=C=C), 1780 (δ CR=CH_2), and 1655 (C=C); nmr (ntms): τ 5.1 (m, 2 H), 5.3 (perturbed quintet, J = 1 cps, 2 H), 7.4 (m, 2 H), and 8.30 (s) and 8.4 (d of doublets) totaling 6 H; assignment: 2-methyl-1,4,5-heptatriene (IX).

Anal. Calcd for C_8H_{12}: C, 88.82; H, 11.18. Found: C, 88.74; H, 11.20.

Second component: *rt* 8.8; *ra* (*vide infra*). Analytical glpc (10 ft × 1/8 in column packed with 20% triscyanoethoxypropane on 80–100 Chromosorb W, 85/147-30 for 5 min, then →105 at 48) revealed it to be a mixture of at least three components with retention times 4.4 (15%), 5.1 (60%), and 5.7–6.2 (30%); ir: 1960 (C=C=C), 1740 (weak, C=C), 1625, 1645, and 1690 (C=C, conjugated), and 840 (trisubstituted C=C); uv (methanol): λ_{max} 232 mμ (log ϵ 4.0), shoulder at 252 mμ; nmr (ntms); τ 3.7–4.5 (complex absorption), 5.0 (m), 8.18 and 8.23 (singlets of equal intensity with broad base); assignment: the major component is most likely 2-methyl-2,4,5-heptatriene (X) while the minor components are isomeric conjugated trienes.

Anal. Calcd for C_8H_{12}: C, 88.82; H, 11.18. Found: C, 88.34; H, 11.17.

Third component: *rt* 18.9; *ra* (*vide infra*); ir: 1980 (C=C=C) and 1755 (ester C=O); nmr (ntms): τ 5.1 (m, 2 H), 7.6 (perturbed d of doublets, 2 H), 8.11 (s, 3 H), 8.4 (d of doublets, 3 H), 8.62 (s, 6 H); assignment: 2-methyl-4,5-heptadien-2-yl acetate (VId).

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.58. Found: C, 70.93; H, 9.53.

The relative abundances of these compounds were determined by preparative glpc peak areas (uncorrected), owing to the fact that no analytical column could be prepared that did not cause substantial elimination of the tertiary ester to give the hydrocarbons. This was not the case on the preparative column, however, each component being stable to the separation conditions. However, the precision is estimated to be ±5%. The data are listed in Table V.

Acetolysis of Vc. A solution of 30 g (88 mmol) of Vc in 500 ml of preparative acetolysis solvent was heated to 65° for 3 hr (15 half-lives), then worked up as usual. Preparative glpc gave the same components as did Vb in essentially the same amounts (Table V). When optically active Vc was subjected to the same conditions, and the products isolated, they showed the following specific rotations: first component $[\alpha]^{25}D$ −1.5° (*c* 3, ethanol); third component $[\alpha]^{25}D$ −2.6° (*c* 2, ethanol).

Stability of Acetolysis Products under Reaction and Isolation Conditions. Small samples (~0.1 g) of each component, and unrearranged ester Vd (not observed as a product) were placed in separate ampoules to which was added 2 ml of acetolysis solvent. The tubes were sealed and heated to 50° for 2.25 hr. Each solution was cooled and worked up in the usual manner, and subjected to analytical glpc. Components 1 and 2 and Vd were unchanged, but tertiary ester VId had undergone ~60% elimination to the hydrocarbons. Some of this decomposition took place on the glpc column.

Test for Return of Vc. A sample of the brosylate was subjected to acetolysis conditions of 65° for 1000 sec (one half-life). The unreacted brosylate was recovered by extraction as usual. An nmr spectrum was identical with the starting material, contaminated with a small amount of the rearranged acetate.

Hydrolysis of Vb (Preparation of VIa). A solution of 12.1 g of Vb in 200 ml of 50% (volume) aqueous acetone containing 20 g of pyridine was warmed to 50° for 48 hr. After cooling, the solution was extracted with a total of 100 ml of ether, which was then washed with 2% acetic acid, 5% sodium bicarbonate, and finally water. After drying (molecular sieves) most of the solvent was removed by careful rotary evaporation. Analytical glpc (95/100-30) showed the following components (by comparison of retention times with those of the acetolysis product): 2.1 min (6%), 2-methyl-1,4,5-heptatriene (IX); 2.6 min (trace), unidentified hydrocarbon; 3.7 (8%), 2-methyl-2,4,5-heptatriene (X); 6.8 (86%), *not* 2,2-dimethyl-3,4-hexadienol. The last component was isolated by careful microdistillation, yielding 3.0 g of a clear colorless liquid, bp 69–71° (13.3 mm); ir: 3300 (broad, OH), 1970 (C=C=C), and 1390 (*gem*-dimethyl); nmr (ntms): τ 5.0 (complex absorption, 2 H), 7.07 (broad s, 1 H), 7.90 (perturbed d of doublets, 2 H), 8.38 (d of doublets, 3 H), 8.82 (s, 6 H); assignment: 2-methyl-4,5-heptadien-2-ol (VIa).

Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.16; H, 11.18.

2-Methyl-4,5-heptadien-2-yl 3,5-Dinitrobenzoate (VIe). The following steps were carried out under a blanket of dry nitrogen. To a magnetically stirred solution of 2.52 g (20 mmol) of VIe in 20 ml of dry tetrahydrofuran was added (*via* syringe and septum) 12.3 ml (~20 mmol) of a solution of 1.6 *M* butyllithium in hexane. After stirring 1 hr, the mixture was cooled in a Dry Ice–acetone bath and a solution of 4.8 g (22 mmol) of freshly recrystallized (carbon tetrachloride) 3,5-dinitrobenzoyl chloride in 10 ml of dry tetrahydrofuran was admitted dropwise. The deep red mixture was allowed to warm to room temperature and stir overnight. The solution was refluxed 2 hr, then while still warm, the solvent was removed at the rotary evaporator. The residue was suspended in 40 ml of ether, and the suspension filtered to remove inorganic salts. Removal of the ether left an oil which was recrystallized four times from 90% petroleum ether (bp 30–60°)-ether, yielding 2.4 g (38%) of pale yellow crystals, mp 55.5–56.5°; ir: 3100 (aromatic CH), 1980 (C=C=C), 1740 (ester C=O, conjugated), 1640 (aromatic C=C), and 1550 and 1350 (NO_2); nmr (ntms): τ 0.87 (perturbed t, J = 2 cps, 1 H), 0.98 (perturbed d, J = 2 cps, 2 H), 5.0 (m, 2 H), 7.4 (perturbed d of doublets, 2 H), and 8.34 (s and m totaling 9 H).

Anal. Calcd for $C_{15}H_{16}N_2O_6$: C, 56.35; H, 5.04. Found: C, 56.40; H, 5.00.

Hydrolysis of VIe. The ester (1.0 g) was dissolved in 100 ml of 65% aqueous dioxane and the solution was heated to 85° for 7.0 days (four half-lives). After cooling, the solution was extracted with 125 ml of ether, which was then washed with 5% sodium bicarbonate and saturated sodium chloride solution. When dry, the solution was analytically gas chromatographed (95/100-30) showing peaks at 2.1 min (IX), 2.6 min (unidentified hydrocarbon), 3.7 min (X), and 6.8 min (VIa), but solvent (dioxane) made determination of the first component difficult. Most of the solvent was removed by careful rotary evaporation, and the remaining yellow solution was rechromatographed. The approximate composition was 2.1 min (70%), 2.6 min (2%), 3.7 min (3%), and 6.8 min (25%). Again, however, dioxane prevented exact determination of the relative amount of the first component.

3-Methyl-3-buten-1-yl Tetrahydropyranyl Ether. A mixture of 34.4 g (0.40 mol) of 3-methyl-3-buten-1-ol and 44 g (0.50 mol) of 2,3-dihydropyran was cooled to 0° and 0.5 g of concentrated hydrochloric acid was added with stirring. When the evolution of heat had ceased, the mixture was heated over steam for a period of 4 hr, then cooled and diluted with 200 ml of ether. The ethereal solution was washed with 5% sodium bicarbonate to pH ~9, then with saturated sodium chloride solution. After drying and solvent removal, careful distillation (to preclude foaming) gave 64 g (95%) of the tetrahydropyranyl ether, bp 53–55° (1.4 mm); ir: (no OH), 3080 (shoulder, $=CH_2$), and 1660 ($C=CH_2$); nmr (ntms): τ 5.30 (sharp m, 2 H), 5.50 (sharp m, 1 H), 6.0–6.9 (complex m, 4 H), 7.76 (t, J = 7 cps, 2 H), 8.27 (s, 3 H), and 8.4 (envelope, 6 H).

Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.54; H, 10.66. Found: C, 70.50; H, 10.79.

3-Methyl-3,4-pentadien-1-yl Tetrahydropyranyl Ether. To a mechanically stirred slurry of 113 g (1.0 mol) of potassium *t*-butoxide in 1-l. of dry pentane cooled in an ice–water slurry, was added 54.7 g (0.32 mol.) of 3-methyl-3-butenyl tetrahydropyranyl ether. Over a period of 5 hr, 162 g (0.64 mol) of fresh bromoform was added with the mixture still at 0°. After addition was completed, the mixture was stirred overnight at ambient temperature. After hydrolysis with 500 ml of water the pentane layer was separated, and the aqueous phase containing some solid material extracted with a total of 100 ml of pentane. The combined pentane solutions were washed with water until the washings were clear, then with saturated sodium chloride solution, and finally dried over sieves. Removal of solvent and excess bromoform at 0.5 mm left 132 g of the crude dibromocyclopropane as a dark oil. The crude product could not be distilled, and was used without further purification.

The crude dibromocyclopropane was dissolved in 150 ml of dry (sodium hydride) ether, and the magnetically stirred solution was cooled to −78° under a stream of dry nitrogen. Cautiously 380 ml of 1.6 *M* methyllithium in ether (0.38 mol) was added over a period of 1.5 hr. After an additional 1.5 hr at −78°, the solution was allowed to warm to ambient temperature and stir for 1 hr. Water (150 ml) was carefully added, the ether phase separated, and the aqueous phase extracted with 100 ml of ether. Combined organic phases were washed with saturated sodium chloride solution, then dried. Removal of solvent and careful distillation gave 40 g (60% for the two-step process) of a clear liquid, bp 58–60° (0.45 mm). Analytical glpc (120/150-30) showed one major peak at 20.5 min representing 96% of the product; ir: (no OH) and 1970 (C=C=C); nmr (ntms): τ 5.45 (m containing q, J = 3 cps, 3H), 6.0–6.8 (complex absorption, 4 H), 7.80 (heptet, J = 3.5 cps, 2 H), and 8.1–8.7 (m containing t at 8.30, J = 3 cps, totaling 9 H).

3-Methyl-3,4-pentadien-1-ol (VIIa). The allenic tetrahydropyranyl ether (36.5 g, 0.20 mol) was dissolved in 300 ml of anhydrous ethanol containing 0.8 g of *p*-toluenesulfonic acid. After refluxing 1.8 hr, the slightly brown solution was cooled, 0.5 g of sodium bicarbonate added, and the solvent removed under reduced pressure. The residue was dissolved in 200 ml of ether, washed with saturated sodium chloride solution, then dried. After the solvent was removed, distillation through a spinning-band column gave 11.5 g (59%) of VIIa, bp 61–64° (11.1 mm). A side product, 2-ethoxytetrahydropyran [6.5 g, bp 39° (11.1 mm)], was also collected during the distillation. The allenic alcohol gave the following spectral characteristics; ir: 3400 (broad, OH), 3050 (shoulder, $=CH_2$), and 1970 (C=C=C); nmr (ntms): τ 5.44 (q with fine structure, J = 3 cps, 2 H), 5.99 (sharp s, 1 H), 6.40 (t, J = 7 cps, 2 H), 7.87 (septet, J = 3 cps, 2 H), 8.33 (t, J = 3 cps, 3 H).

Anal. Calcd for $C_6H_{10}O$: C, 73.43; H, 10.27. Found: C, 73.34; H, 10.14.

3-Methyl-3,4-pentadien-1-yl tosylate (VIIb) was prepared in 90% yield by the usual method. The oil solidified on standing at −20°, but melted upon reaching ambient temperature; ir: (no OH), 1970 (C=C=C), 1610 (aromatic C=C), and 1375 ($-SO_2-$); nmr (ntms): τ 2.23 (perturbed d, J = 8 cps, 2 H), 2.65 (perturbed d, J = 8 cps, 2 H); 5.42 (q, J = 3 cps, 2 H); 5.91 (t, J = 7 cps, 2 H), 7.59 (s) and 7.75 (septet, J = 3 cps) totaling 5 H, and 8.40 (t, J = 3 cps, 3 H).

Anal. Calcd for $C_{13}H_{16}O_3S$: C, 61.89; H, 6.39. Found: C, 61.84; H, 6.49.

3-Methyl-3,4-pentadien-1-yl brosylate (VIIc) was prepared in 85% yield; it was an oil which solidified on standing at −20°. The melting point of the glass-like material was ~33°; ir: 1980 (C=C=C), 1590 (aromatic C=C), and 1380 ($-SO_2-$); nmr (ntms): τ 2.25 (s, 4 H), 5.47 (q, J = 3 cps, 2 H), 5.87 (t, J = 7 cps, 2 H), 7.73 (septet, J = 3 cps, 2 H), and 8.38 (t, J = 3 cps, 3 H).

Anal. Calcd for $C_{12}H_{13}BrO_3S$: C, 45.44; H, 4.13. Found: C, 45.30; H, 4.33.

3-Methyl-3,4-pentadien-1-yl acetate (VIId) was prepared by the usual procedure in 75% yield, bp 65–70° (9 mm); ir: (no OH), 1975 (C=C=C), 1755 (ester C=O), and 1245 (COC, acetate); nmr (ntms): τ 5.37 (q, J = 3 cps, 2 H), 5.86 (t, J = 7 cps, 2 H), 7.75 (septet, J = 3 cps, 2 H), 8.02 (s, 3 H), and 8.27 (t, J = 3 cps, 3 H).

Anal. Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 67.86; H, 9.02.

Acetolysis of VIIb. A solution of 11.0 g of VIIb in 250 ml of preparative acetolysis solvent was warmed to 85° for 5.00 days (*ca.* seven half-lives). The solution was worked up in the usual manner, and the dried solution of acetolysis products subjected to analytical glpc (90/128-30). Only three components were indicated with retention times 4.3 min (56%), 7.0 min (1.4%), and 9.3 min (43%). The retention time of authentic VIId under these conditions was 9.4 min. Preparative glpc was abandoned in favor of microfractionation, which gave the following results.

First fraction: bp 44–46° (12 mm); analytical glpc indicated less than 2% impurities; ir: 3090 (=CH_2), 1750 (ester C=O), 1695 (exocyclic C=C), 1255 (acetate COC), and 895 (1,1-disubstituted double bond); nmr (ntms): τ 4.92 (t, J = 2.5 cps, 1 H), 5.23 (t, J = 2.0 cps, 1 H), 7.4–8.0 (complex envelope, 4 H), 8.08 (s, 3 H), and 8.49 (s, 3 H); assignment: 1-methyl-2-methylenecyclobutyl acetate (XI).

Anal. Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.70; H, 8.66.

Second fraction: bp 55–57° (11 mm); analytical glpc showed three peaks: 4.1 min (19%), 7.0 min (5%), and 9.3 min (76%); ir: very similar to that of the unrearranged acetate (VIId), except the allene stretch (1975 cm^{-1}) was much less intense in comparison to the C=O absorption; nmr (ntms) subtracting the absorptions due to XI (19%) and VIId (20%) left the following: τ 5.60 (s, 2 H), 7.68 (s, 4 H), 8.03 (s, 3 H), and 8.30 (s with additional fine structure which is probably due to the methyl triplet of VIId, 3 H). A second chromatography 6 ft × $^1/_8$ in. column packed with 15% Carbowax 20M on 80–100 Chromosorb W (115/150-30) separated XII (*rt* 7.7, *ra* 70%) from VIId (*rt* 9.0, *ra* 30%); assignment: 1-acetoxymethyl-2-methylcyclobutene (XII).

Anal. Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.66; H, 8.44.

When a sample of the tosylate (VIIb) was allowed to undergo acetolysis at 65° for 6.0 days (1.5 half-lives), the product ratios were: first component 74%, third component 26% (no second component at 7.0 min was observed, indicating that it represents an ester which arises through rearrangement of one of the primary products). Assuming that the fraction of VIId in the third component was the same as for the run at higher temperature (*vide supra*), the latter 26% was composed of 11% VIId and 15% XII.

Test for Return of VIIb. A sample of VIIb (6.0 g) was dissolved in 200 ml of preparative acetolysis solvent and heated to 65°. After 6.0 days (1.5 half-lives), the solution was cooled and worked up as usual. After analysis of the solution for acetolysis products by glpc, the solvent and all volatile materials were removed under reduced pressure. Only a yellow oil remained, the nmr spectrum of which was identical with that of the starting tosylate.

Isopulegone Ethylene Ketal. A solution of 45.2 g (0.3 mol) of technical (+)-pulegone, 27.9 g (0.4 mol) of ethylene glycol, and 0.4 g of *p*-toluenesulfonic acid in 450 ml of dry toluene was distilled slowly through a vacuum-jacketed 50-cm column. Additional dry toluene was added during the distillation to maintain the original volume. When 1 l. of distillate had been collected (bp 108–110°), the pot mixture was cooled and diluted with 500 ml of ether. This solution was washed with 5% sodium bicarbonate and saturated sodium chloride, then dried over sieves. Removal of solvent left a golden oil which, upon distillation, yielded 35 g of impure ketal. Analytical glpc (Carbowax column, 150/185-34) showed the desired ketal (7.8 min, 70%) together with pulegone (6.8 min, 25%) and an isomeric ketal at 9.0 min. Because the desired ketal could not be separated from the impurities even by distillation through a spinning-band column, the material was dissolved in 400 ml of dry toluene containing 20 g of ethylene glycol and 0.1 g of *p*-toluenesulfonic acid, and distilled as before until 700 ml of distillate had been collected. Work-up as before, then distillation afforded 31 g, bp 50–55° (0.58 mm) [lit.[10,11] 62° (0.7 mm)], which was 87% pure by glpc. This material was used without further purification; ir: 3030 (=CH_2), no C=O, 1180, 1160, 1145, and 1075 (cyclic ketal); nmr (ntms): τ 5.25 (d, J = 1 cps, 2 H), 6.23 (s, 4 H), 7.7–8.5 (complex absorption containing t, J = 1 cps, at τ 8.24, totaling 10 H), and 8.9–9.3 (m containing d at τ 9.12, J = 6, total area 4 H).

5-Methyl-2-(1-methylpropadienyl)cyclohexanone Ethylene Ketal. Using a method identical with the preparation of 3-methyl-3,4-pentadienyl tetrahydropyranyl ether, 36 g (0.18 mol) of the 87% pure isopulegone ketal was allowed to react with 61.5 g (0.54 mol) of potassium *t*-butoxide and 91 g (0.36 mol) of bromoform. Work-up as before left 71 g of the crude dibromocyclopropane derivative. This was not purified further, but was treated with 110 ml of 1.6 *M* methyllithium in ether. Hydrolysis followed by distillation gave 20.1 g (54% for the two-step process) of a clear colorless liquid, bp 64–72° (0.58 mm) [lit.[10,11] 62° (0.4 mm)]. Analytical glpc (Carbowax column, 150/185-34) showed a peak at 13.0 min representing >90% of the product; ir: 1950 (C=C=C) and 850 (=CH_2); nmr (ntms): τ 5.50 (q, J = 3 cps, 2 H), 6.17 (s, 4 H), 8.0–8.8 (complex absorption containing t at τ 8.26, J = 3 cps, total area 10 H), and 8.9–9.3 (m containing d at τ 9.10, J = 6 cps, totaling 4 H).

5-Methyl-2-(1-methylpropadienyl)cyclohexanone. To a solution of the allenic ketal (20 g, 0.10 mol) in 350 ml of dioxane was added 50 ml of 1 *N* perchloric acid, and the solution was stirred at ambient temperature for 26 hr. Water (300 ml) was added, and the solution was extracted with a total of 500 ml of ether. Removal of solvents and distillation gave 11.5 g (73%) of a pale yellow liquid, bp 59–64° (0.68 mm) [lit.[10,11] 56° (0.7 mm)]. Analytical glpc (Carbowax column, 150/185-34) showed one major peak at 11.6 min representing 94% of the product. The remainder was divided among five impurities of lower retention time; ir: 1950 (C=C=C), 1715 (C=O), 1640 (very weak, conjugated isomers), and 850 (=CH_2); nmr (ntms): τ 5.44 (q with fine structure, J = 3 cps, 2 H), 7.1–7.5 (envelope, 1 H), 7.5–9.4 [envelope containing t at 8.35 (J = 3 cps) and sharp m at 9.0 totaling 13 H (theoretical 13 H)].

5-Methyl-2-(1-methylpropadienyl)cyclohexanol (VIIIa). To a suspension of 1.2 g (31 mmol) of lithium aluminum hyride in 100 ml of dry ether was added 10.2 g (61 mmol) of the allenic ketone in 100 ml of dry ether over a period of 3 hr. The solution was stirred 22 hr at ambient temperature, then carefully hydrolyzed and worked up in a manner analogous to the preparation of Va. Removal of the ether and subsequent distillation afforded 8.0 g of a clear colorless liquid, bp 67–71° (1.5 mm). Analytical glpc (Carbowax column, 150/185-34) showed two major peaks at 10.3 min (14%) and 11.5 min (70%). The remainder was partitioned between three components: 6.0 min (2%), 7.0 min (5%), and 14.2 min (7%). The mixture was slowly redistilled and two cuts were taken: I, 2.2 g, bp 69–70° (1.4 mm), glpc showing 86% of the two major components and 14% of side products with shorter retention times; II, 3.3 g, bp 70–71° (1.4 mm), glpc showing 98% of the two major components in the ratio 1:5. The pot residue (~2 g) proved to be 75% of the two major components, and 25% of material with a higher retention time. The material in the second cut (two isomers in the ratio 1:5) gave the following spectra; ir: 3500 and 3400 (sharp, OH), 1950 (C=C=C), 1640 (~ half as intense as the band at 1950, conjugated C=C), and 850 (=CH_2); nmr (ntms): τ 5.4 (q, J = 3 cps, 2 H), 5.9–6.9 (complex envelope, 1 H), 7.4 (broad absorption, 1 H), 7.8–9.4 [complex envelope containing t at 8.33 (J = 3 cps) and d at 9.1 (J = 3 cps)]; uv (methanol): λ_{max} 255 mμ [log ϵ (based on the minor component) 3.57]; assignment: the major component is the desired cyclic allenic alcohol (VIIIa), with –OH equatorial based on the similarity of the absorption due to the proton geminal to the hydroxyl group to the analogous proton in l-menthol.[13,14] The minor component is *not* the corresponding epimer (–OH axial), but rather a conjugated isomer.

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.05; H, 11.01.

Tosylate of VIIIa. A solution of 1 equiv of VIIIa and 1.4 equiv of *p*-toluenesulfonyl chloride in dry pyridine was allowed to stand at −20° for 48 hr. The resulting red solution was worked up as usual. Removal of solvent and volatile impurities left 0.7 equiv of an orange oil. The tosylate could not be completely freed from unreacted alcohol as the spectra indicate. Therefore the kinetics were calculated on the basis of infinity titer rather than initial substrate concentration; ir: 3500 (sharp, ~$^1/_4$ as intense as the absorption at 1950), 1950 (C=C=C), 1600 (aromatic C=C), 1370 (–SO_2–), 850 (=CH_2); nmr (ntms): τ 2.28 (perturbed d, J = 8 cps, 2 H), 2.73 (perturbed d, J = 8 cps, 2 H), 5.6 (m, 2 H), 6.0–6.8 (m), 7.60 (s, 3 H), 8.0–9.5 [envelope containing t at 8.33 (due to alcohol), t at 8.52 (J = 3 cps) and m at 9.1].

Anal. Calcd for $C_{18}H_{24}O_3S$: C, 67.48; H, 7.55. Found: C, 68.86; H, 8.15.

Acetate VIIId was prepared by the usual method (reflux time 4 hr). Short-path distillation gave a 70% yield of a clear colorless liquid, bp 70–72° (0.6 mm). Analytical glpc (Carbowax column, 150/185-34) showed two peaks: 9.0 min (80%) and 11.8 min (20%); ir: (no OH), 1960 (C=C=C), 1740 (ester C=O), and 850 (=CH_2); nmr (ntms): τ 5.45 (q, 2 H), 6.2–6.5 (m, 1 H), and 7.8–9.6 [envelope containing s at 8.12 (with shoulder), t at 8.4 (J = 3 cps) and d at 9.0 (J = 4 cps)]; assignment: the major product is the authentic acetate VIIId; the minor component is presumably the acetate corresponding to the conjugated impurity in VIIIa.

Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 75.16; H, 9.81.

Acetolysis of VIIIb. A solution of 2.8 g of the tosylate in 50 ml of preparative acetolysis solvent was warmed to 85° for 19 hr (eight half-lives), then worked up as usual. Analytical glpc (Carbowax column, 150/185-34) showed one broad peak at 9.0 min, with at least two shoulders at slightly higher retention time. This peak represented greater than 96% of the product mixture. Distillation of the product mixture gave 1.0 g of a clear colorless liquid, bp 68–71° (0.7 mm), the glpc of which still showed at least three components; ir: virtually identical with authentic VIIId, with slight variations in relative intensities. In addition to the absorptions attributable to VIIId, the following nmr peaks were observed (ntms): τ 4.98 (d, J = 3 cps), 5.22 (d, J = 3 cps), 5.64 (broadened s), 8.15 (s), 8.16 (s), 8.41 (s), and 8.64 (s); assignment: because of the complexity of this spectrum and the inability to effectively separate the components, these assignments should be considered tentative. Elemental analysis and spectral comparison with products from VIIb indicate that the three major products are those indicated in eq 4. The approximate ratios were estimated from the nmr integration.

Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 76.19; H, 9.89.

Test for Return of VIIIb. After 3000 sec (one half-life) a 5-ml aliquot was withdrawn from the above preparative acetolysis mixture. Work-up as usual left a yellow oil, the nmr spectrum of which was identical with that of starting material. The main impurity was unreacted VIIIa, the amount of which had increased with respect to the tosylate.

Tosylates of Saturated Alcohols. Using the usual method, 20 mmol of the respective alcohol was allowed to react with 4.2 g (24 mmol) of *p*-toluenesulfonyl chloride. The products were oils which were not purified further. The ir spectra of these tosylates were all virtually identical, showing only the expected bands. The yields and nmr spectral values for each is given below.

***n*-Amyl tosylate**: 91%; (ntms): τ 2.30 (perturbed d, J = 8 cps, 2 H), 2.71 (perturbed d, J = 8 cps, 2 H), 6.07 (t, J = 6 cps, 2 H), 7.58 (s, 3 H), and 8.3–9.3 (complex envelope containing sharp peak at 9.15, 9 H).

Anal. Calcd for $C_{12}H_{18}O_3S$: C, 59.49; H, 7.49. Found: C, 59.47; H, 7.46.

***n*-Hexyl tosylate**: 92%; (ntms): τ 2.27 (perturbed d, J = 8 cps, 2 H), 2.68 (perturbed d, J = 8 cps, 2 H), 6.04 (t, J = 6 cps, 2 H), 7.58 (s, 3 H), 8.2–9.4 (complex envelope, 11 H).

Anal. Calcd for $C_{13}H_{20}O_3S$: C, 60.92; H, 7.87. Found: C, 60.83; H, 7.87.

***n*-Heptyl tosylate**: 80%; (ntms): τ 2.25 (perturbed d, J = 8 cps, 2 H), 2.67 (perturbed d, J = 8 cps, 2 H), 6.03 (t, J = 6 cps, 2 H), 7.60 (s, 3 H), and 8.1–9.4 (complex envelope, 13 H).

Anal. Calcd for $C_{14}H_{22}O_3S$: C, 62.20; H, 8.20. Found: C, 62.42; H, 8.06.

2-Hexyl tosylate: 85%; (ntms): τ 2.30 (perturbed d, J = 8 cps, 2 H), 2.73 (perturbed d, J = 8 cps, 2 H), 5.47 (q, J = 6 cps, 1 H), 7.60 (s, 3 H), 8.3–9.1 (envelope) and 8.80 (d, J = 6) totaling 9 H, and 9.2 (m, 3 H).

Anal. Calcd for $C_{13}H_{20}O_3S$: C, 60.92; H, 7.87. Found: C, 60.53; H, 7.76.

2-Methyl-2-butyl 3,5-Dinitrobenzoate. Using the same procedure as for the preparation of VIe, the ester was synthesized in 64% yield, mp 115.5–117° (lit.[29] 117°); ir: 3100 (aromatic CH), 1740 (ester C=O), and 1640 (aromatic C=C); nmr (acetone-d_6, ntms): τ 0.97 (m, 3 H), 8.0 (m, 2.8 H), 8.37 (s, 6 H), and 9.0 (t, J = 7 cps, 3 H).

Anal. Calcd for $C_{12}H_{14}N_2O_6$: C, 51.06; H, 5.00. Found: C, 51.05; H, 4.99.

Acetolysis Kinetic Determinations. A sample of the sulfonate ester (~5 mmol) was precisely weighed by difference into a 50-ml volumetric flask, which was then filled to the mark with kinetic acetolysis solvent (*vide infra*) at ambient temperature. The flask was vigorously shaken, then ~5.5-ml portions of the solution were pipetted into each of nine ampoules, which were then frozen in Dry Ice–acetone and sealed. The ampoules were placed in an oil bath at the desired temperature, and upon reaching bath temperature (t = 0 sec) one was removed, quenched in Dry Ice–acetone, warmed to ambient temperature, then cracked open. Exactly 5.00 ml was removed and titrated with standard perchloric acid (*vide infra*) to crystal violet end point. Similarly the remaining ampoules were removed at timed intervals and similarly titrated. From the titration values were calculated the rate constants and associated kinetic parameters by use of a FORTRAN IV computer program and an IBM 360-75 computer.

The kinetic acetolysis solvent was prepared as follows: fresh glacial acetic acid was refluxed 4 hr with 2% added acetic anhydride, then distilled. To 1 l. of the dry acid was added 1.5 g of acetic anhydride (0.01 *M*) and 9.0 g anhydrous sodium acetate (providing an acetate ion concentration of 0.11 *M*). The standard perchloric acid (0.10 *M*) was prepared by dissolving 3.7 g of 70% perchloric acid in 250 ml of dry acetic acid. This was standardized against a solution of exactly known acetate ion concentration, formed by the reaction of a carefully weighed amount of dry lithium carbonate with dry acetic acid. The carbonic acid was removed by gently refluxing under anhydrous conditions. All solutions were kept scrupulously free of moisture.

Preparative Acetolysis Solvent. To 1 l. of dry acetic acid (*vide supra*) was added 1.5 g of acetic anhydride and 17 g of anhydrous sodium acetate, to provide an acetate ion concentration of 0.2 *M*.

Hydrolysis Kinetic Determinations. Hydrolysis kinetics of the 3,5-dinitrobenzoates were followed using the ampoule technique described above, but the solvent was 65% (v/v) aqueous dioxane. The titrant consisted of 0.4 g of sodium hydroxide in 500 ml of 65% aqueous dioxane, and it was standardized daily against 3,5-dinitrobenzoic acid to bromothymol blue end point. About 1.0 mmol of the ester was weighed accurately into a 50-ml volumetric flask, and after dilution to the mark, nine ampoules were filled and the run was begun as in the acetolyses. The volume of titrant required at t = 0 was subtracted from each of the succeeding values. The data were evaluated by a computer program similar to the one mentioned above.

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