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ADDITIONAL EVIDENCE FOR HOMOALLENYL PARTICIPATION

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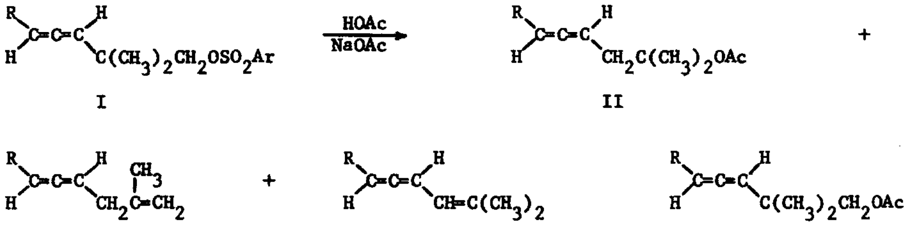
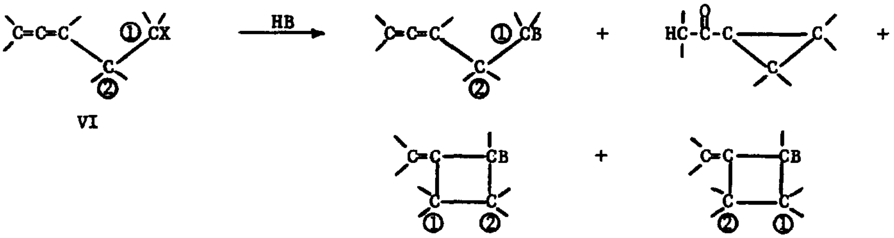
It was recently reported(2) that a properly located allenyl system, $>C=C=C<$, accelerated solvolysis more than a similarly located carbon-carbon double bond. Acetolysis of allenic brosylate Ia gave a first order rate constant (TABLE II) which was 19 times greater than that of 2,2-dimethyl-3-buten-1-yl brosylate(3) and 5600 times that of 2,2-dimethyl-1-pentyl brosylate(4). Rearranged products IIa (77%), IIIa (12%), and IVa (11%) were formed, and no products having the unrearranged carbon skeleton, such as acetate Va, were detected. It has also been reported that



I II III IV V

Ia-Va: R=H, Ar= p-BrC_6H_4; Ib-Vb: R=CH_3, Ar= p-BrC_6H_4; Ic-Vc: R=CH_3, Ar= p-$CH_3C_6H_4$.

similar allenyl systems, VI, bearing other substituents, yield unrearranged products(5,6), cyclopropyl ketones(5,6), and cyclobutyl derivatives(6). These experiments indicate that the allenic



VI

system has the same versatility as the double bond for participation in solvolyses, and that similar interpretations should be applicable(7,3).

Because appropriately substituted allenyl alcohols of general structure VI can be at least partially resolved fairly easily(8), several such compounds have been synthesized in our laboratory for examination of addition reactions. The solvolytic reactivities of these compounds are also being investigated. This paper concerns the acetolysis of the brosylate Ib and tosylate Ic of 2,2-dimethyl-3,4-hexadienol.

Acetolysis of Ib, using essentially the conditions of Bly(3), gave three principal products which were separated by g.l.c. and isolated. Vb was not found among these products, although a sample prepared directly from the alcohol was stable under the reaction and separation conditions. Two of the products were identified by IR, NMR, and elemental analysis as IIb and IIIb. The third component was rechromatographed, revealing it to be a mixture of three compounds in the ratio of 5:2:1. Elemental analysis was in agreement with the empirical formula C_8H_{12}. A strong band in the IR spectrum at 1960 cm^{-1} was evidence for the presence of an allenic compound as the major component of the mixture. Structure IVb is suggested on the basis of the ultraviolet spectrum (λ_{max} 232 mμ, log ε ~ 4) and analogy with the results from Ia. A shoulder at 252 mμ suggests that the other components of the mixture could 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. Strong methyl peaks at 8.18 and 8.23 τ appeared to be singlets, but resolution was incomplete and greater multiplicity could have been obscured by the broad nature of the bottom of the peaks. The olefinic region was complex; absorption lay at 3.7 - 4.5 τ (olefinic protons) and 4.8 - 5.4 τ (allenic and possible olefinic protons). Isolation of the individual components of the mixture was not achieved because amounts available were small and the mixture polymerized rapidly even at 0°. Inclusion of conjugated trienes as components would be expected to give ready polymerization. Such trienes might arise from rearrangement of IIIb and IVb, even though it was shown that the composition of the mixture was unchanged when a sample was rechromatographed. Formation of 2,5-dimethyl-1,3-hexadiene as a minor product from the acetolysis of 2,2,4-trimethyl-3-penten-1-yl brosylate(3) represents a similar rearrangement. Compound IIIb was stable to the conditions employed, but tertiary ester IIb tended to eliminate acetic acid to form IIIb and IVb. Similar difficulties were observed by Bly and Swindell(3). TABLE I gives the product ratios. Tosylate Ic gave very similar results.

TABLE I[a]

Acetolysis Product Ratios

Cmpd	Reaction Time[b]	IIb	IIIb	IVb	Other[c]
Ib	6	45	25	19	11
Ib	10	55	16	18	11
Ic	5	49	23	18	10
Ic	8	54	20	16	10

[a] Temp. 65°; values from uncorrected g.l.c. peak areas.

[b] In half-lives.

[c] Two components, probably conjugated trienes, in the ratio 2:1

The kinetics of the acetolyses, followed titrametrically to about 80% completion, are cleanly first order. The rate constants and activation parameters are given in TABLE II. Related values are given for comparison.

TABLE II[a]

Acetolysis Kinetic Data

Cmpd	T°C	k sec^{-1}	ΔF* $\frac{kcal}{mole}$	ΔH* $\frac{kcal}{mole}$	ΔS* e.u.
Ia[b]	40.0 54.7 70.1	1.80×10^{-5} 9.85×10^{-5} 4.88×10^{-4}		22.5	-8.3
Ib	40.0 50.1 65.0	6.43×10^{-5} 2.13×10^{-4} 9.93×10^{-4}	24.37 24.41 24.53	22.4[c]	-6.3
Ic	40.0 50.0 65.0	1.83×10^{-5} 5.96×10^{-5} 3.21×10^{-4}	25.15 25.22 25.29	23.5[d]	-5.6
VII[e]	59.7 74.6 90.9	9.40×10^{-8} 6.99×10^{-7} 4.85×10^{-6}		29.9	-0.84

[a] Best linear fits were determined by least squares calculations. [b] Ref. (2). [c] E* = 22.95 kcal/mole. [d] E* = 24.06 kcal/mole. [e] 2,2-dimethyl-1-hexanyl brosylate; data from Ref. (4).

Finally, the acetolysis of optically active Ib, $[\alpha]_D^{25}$ -2.7° (from (-)-2,2-dimethyl-3,4-hexadienol(8), $[\alpha]_D^{25}$ -6.6°) gave optically active IIb and IIIb, $[\alpha]_D^{25}$ -2.6° and -3.9° respectively. The mixture of hydrocarbons (> 60% IXb) was also active, $[\alpha]_D^{25}$ -1.5°. Optically pure Ib was not available for these experiments, but the results indicate that the solvolysis is at least partially stereospecific, and to this extent cannot proceed through a symmetrical intermediate or transition state at any stage.

Our results are in agreement with those of Bly and Koock(2). A methyl group at the end of the allenyl system appears to increase electron availability in the more distant π-cloud or on the central carbon of the allenyl group with resultant increases on the solvolytic rates of 3 to 4 times. The tosylate is about one-third as fast as the brosylate, as expected. The nature of the intermediate ion or ions that intervene between arylsulfonate I and solvolysis products is not clarified by the work completed so far. Bicyclobutonium ion(7) may be involved, but less delocalized ions, such as those with bisected geometry (VIII and IX), would also account for the

enhanced reactivity and stereospecificy of the solvolysis(3,7,9). It would be particularly interesting in this regard to examine more closely those allenic compounds which yield methylenecyclobutyl products(6). It is hoped that the work presently underway will aid in the elucidation of the mechanism of these and related reactions.

The extent of delocalization provided by the allenyl system, as compared to a vinyl group, is of interest. Comparison of Ia with 2,2-dimethyl-3-buten-1-yl brosylate places a $H_2C{=}C{=}CH-$ group in juxtaposition to $H_2C{=}CH-$, which ignores the influence of the third carbon. The propenyl group would probably be a better model and may be as effective as the allenyl system in promoting solvolyses. It is being examined.

The effect of the terminal methyl group in increasing electron availability in the more distant π-cloud and especially on the central carbon atom of the allenyl group may also suggest a reasonable explanation for the anomalous orientation of addition of hydrogen chloride to 3-methyl-1,2-butadiene(10)

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