

A NOVEL RING CONTRACTION DURING THE VAPOR PHASE PYROLYSIS
OF SUBSTITUTED TRANS-1-HYDROXY-2-ACETOXYCYCLOHEXANES

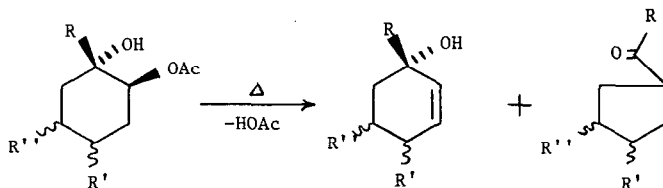
John C. Leffingwell and Ronald E. Shackelford

(Research and Development Departments, R. J. Reynolds Tobacco Company

Winston-Salem, North Carolina 27102)

(Received in USA 25 February 1970; received in UK for publication 20 April 1970)

The vapor phase pyrolysis of a number of terpene hydroxyacetates derived from terpene epoxides has been reported by Royals and Leffingwell to give terpenoid allylic alcohols.¹ During a reinvestigation and extension of this earlier work, we have discovered that pyrolytic ring contractions which produce ketonic products accompany the formation of the previously reported allylic alcohols. We have now demonstrated the generality of such pyrolytic ring contractions by the pyrolysis of five substituted trans-1-hydroxy-2-acetoxycyclohexanes. On pyrolysis these systems all follow the general equation:



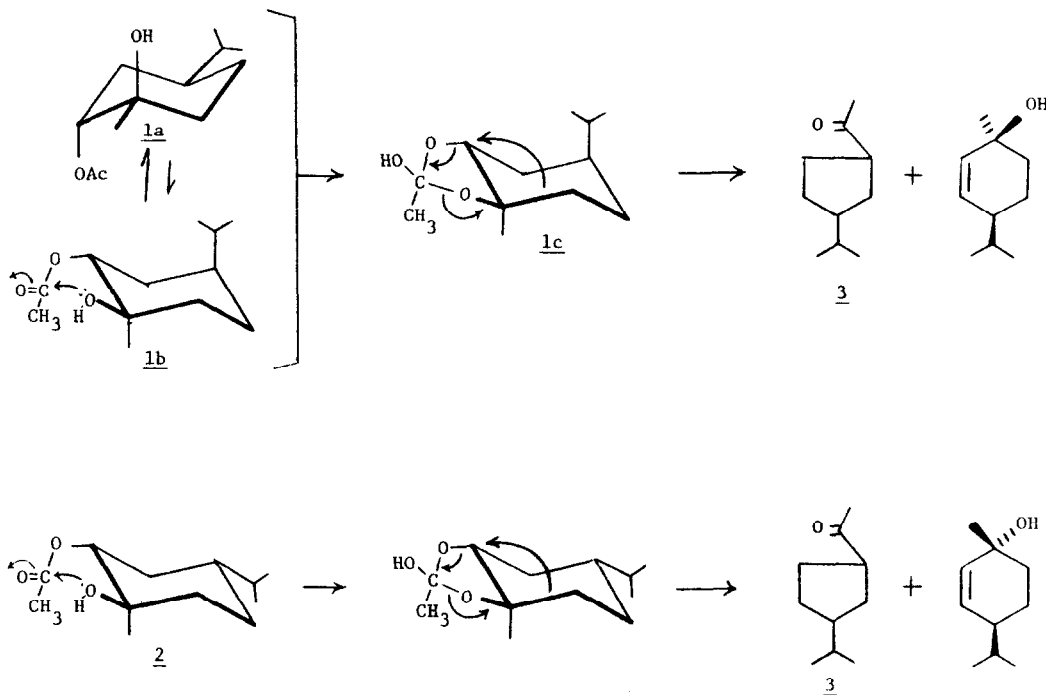
A study of the ratio of ring contracted cyclopentyl alkyl ketones to the alcohols produced over a pyrolysis range of 400-520° indicated no notable temperature dependence on the observed product ratio. The ratio of alcohol to ketone is found in the table.

We propose that ring contraction during these pyrolyses proceeds through neighboring group participation (via conformational interchange when necessary) with pyrolytic collapse of an intermediately formed ortho acid.

T A B L E

<u>Hydroxyacetate Pyrolyzed</u>	<u>Temperature</u>	<u>% Alcohol</u>	<u>Product Ratio</u>	
				<u>% Ring Contracted Ketone</u>
1-Hydroxyneocarvomenthylacetate	449°	77	:	23
1-Hydroxyneoisocarvomenthylacetate	480°	25	:	75
4-Hydroxyneomenthylacetate	444°	35	:	65
1-Hydroxyneodihydrocarvylacetate	480°	70	:	30
3-Hydroxy-4-neocaranylacetate	420°	76*	:	24

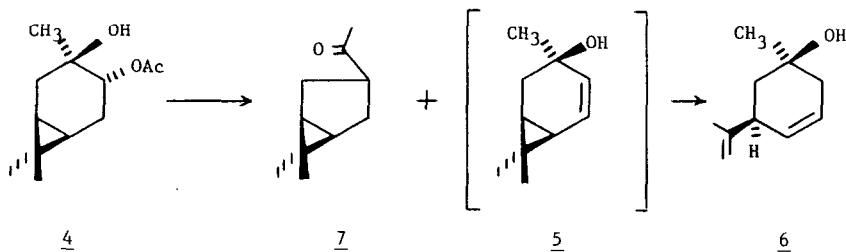
* The alcohol isolated was the thermal rearrangement product, trans-4,8-m-menthadiene-1-ol, 6, rather than the allylic alcohol, 3-hydroxy-4(5)-carene, 5.



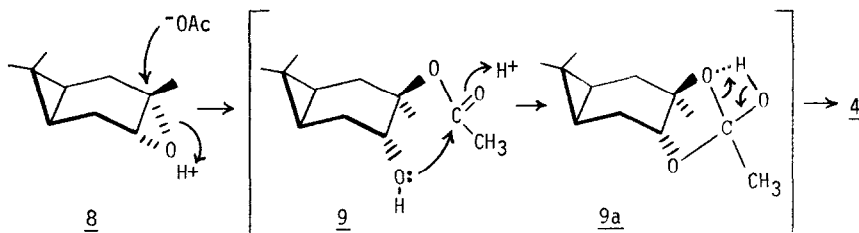
After our initial observation that ring contraction to a ketonic product occurred with 1-hydroxyneocarvomenthylacetate, 1, we reasoned that by choosing an appropriate isomeric trans hydroxyester system that we could increase the percentage of ring contraction during pyrolysis. We predicted that under the pyrolytic conditions employed that the free energy difference that

favors conformation 1a over 1b for 1-hydroxyneocarvomethylacetate must be partially overcome and that the neighboring groups could interact to form an intermediate transition state such as the ortho acid 1c in which the conformational disposition for ring contraction would be very favorable. In the case of the isomeric 1-hydroxyneoisocarvomethylacetate, 2, the hydroxy and ester groups should already be in the more favorable diequatorial positions and thus conformational interchange such as is required in the energetically less favorable case above would not be necessary for neighboring group participation. The experimental observation that hydroxyester 2 affords 3.6 times more of the ketone 3 than the isomeric hydroxyester 1 would appear to support the validity of this reasoning.

The alcohols formed in each of the reported cases arise from a classical acetate pyrolysis mechanism. In the case of 3-hydroxy-4-neocaranylacetate², 4, the initially formed allylic alcohol, 5, was not isolated, but the thermal sigmatropic rearrangement product trans-4,8-menthadiene-1-ol³, 6, was obtained in admixture with the ring contraction product, 6,6-dimethyl-3-acetyl-bicyclo-[3.1.0]-hexane, 7.



The postulate of a neighboring group participation during pyrolytic ring contraction is further supported by the related observation that a similar intermediate ortho acid (9a), as is required for formation of 4, has been indicated as arising during the solvolysis of α -3,4-epoxycarane, 8, with acetate buffered acetic acid.⁴



R E F E R E N C E S

1. J. C. Leffingwell and E. E. Royals, Tetrahedron Letters, 3829 (1965); E. E. Royals and J. C. Leffingwell, J. Org. Chem., 31, 1937 (1966).
2. P. J. Kropp, J. Am. Chem. Soc., 88, 4926, (1966).
3. All new compounds gave appropriate I.R., N.M.R. and mass spectra.⁵
4. J. C. Leffingwell, Ronald E. Shackelford and H. J. Young; manuscript in preparation.
5. The authors gratefully acknowledge Mr. Wm. Walker, Mr. George Young and Mr. John Whalen for spectral data.