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VAPOR PHASE THERMOLYSIS OF 1-HEXEN-5-YN-3-OL. AN ACETYLENIC OXY-COPE REACTION
Alfred Viola and John H. MacMillan, Department of Chemistry, Northeastern University,
Boston, Massachusetts 02115.

1-Hexen-5-yn-3-ol, shown to be free of the internal acetylenic isomer, was subjected to vapor phase thermolysis in a flow system over the range of 350 - 390° and under various pressures. The extent of β -hydroxy-olefin cleavage, which leads to formation of acrolein and allene, was independent of residence time in the thermolysis zone but increased with temperature, indicative of a higher activation energy than the competing rearrangement processes. One of these processes affords 4,5-hexadienal via an acetylenic analog of the oxy-Cope reaction. Also produced is 3-cyclopentenecarboxaldehyde in amounts increasing with increasing temperature and/or increasing residence time. The data is consistent with an electrocyclic reaction involving the enol progenitor of the Cope product, which ketonizes only upon condensation in the product trap.

October 13, 14, 15, 1968

Boston, Massachusetts