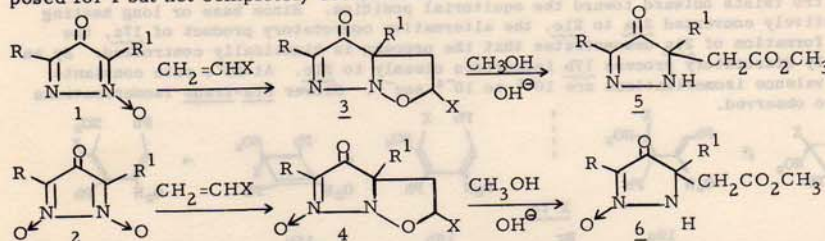


103. CYCLOADDITION REACTIONS OF 3,4-DIAZACYCLOPENTADIENONE OXIDES. Jeremiah P. Freeman, Michael J. Hoare, Department of Chemistry, University of Notre Dame, Notre Dame, Ind. 46556.

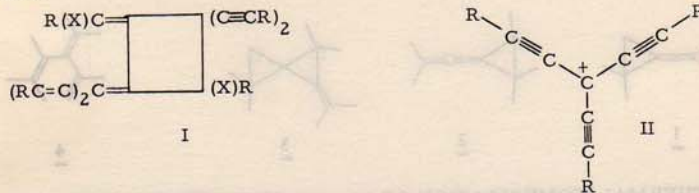
3,4-Diazacyclopentadienone monoxides 1, and dioxides 2 undergo cycloaddition reactions with dipolarophiles to give a new class of heterocyclic compounds. The structure of the monoxide adduct 3 serves to confirm the structure previously proposed for 1 but not completely established.



Both adducts 3 and 4 in which X=CN undergo a base-catalyzed ring opening to yield the α -substituted acetates 5 and 6. Evidence for the structures proposed will be discussed.

104. THE CHEMISTRY OF TRI-*t*-BUTYLETHYNYLCARBINOL AND RELATED ALLENES. Sidney I. Miller, C. K. Tseng, Illinois Institute of Technology, Chicago, Illinois.

Apart from the carbinols, triphenylethyne carbinol, tri-*t*-butylethyne carbinol, and their esters, triethynylmethyl derivatives, $(RC\equiv C)_3CX$, appear to be unknown. Tri-*t*-butylethyne carbinol can be converted to 1,1-di-*t*-butylethyne-3-*t*-butylallenes, $(t-C_4H_9C\equiv C)_2C=C=CX(C_4H_9-t)$, e.g. chloride, bromide, and carboxylic acid. The haloallenes dimerize readily to give one (I) of six possible structures. The tri-*t*-butylethyne carbinol cation (II) has δ CH_3 1.86 and can be prepared from the carbinol in chlorosulfonic acid.



105. THE VAPOR PHASE ACETYLENIC OXY-COPE REACTION OF 5-HEXEN-1-YN-3-OL. THE CHEMISTRY OF AN ALLENOL INTERMEDIATE. Alfred Viola, John H. MacMillan, Northeastern University, Boston, Mass. 02115.

Vapor phase thermolysis of 5-hexen-1-yn-3-ol affords 2- and 3-cyclopentenecarboxaldehydes, trans 2,5-hexadienal and sorbaldehyde. Since β -hydroxyolefin cleavage, which normally competes with oxy-Cope processes, is completely absent, kinetic parameters could be ascertained. E_a and ΔS^\ddagger of the reaction are indicative of a concerted mechanism and suggest that participation of triple bonds in electrocyclic reactions leads to increased rates in comparison with the corresponding olefinic structures. Based upon kinetic data, upon effects of temperature and contact time on product distribution and upon deuterium tracer studies, a reaction scheme is proposed which centers on the intermediacy of the allenol product. The observed compounds, then, represent various reactions of the allenol, 1-hydroxy-1,2,5-hexatriene.

