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THE 1,2 VERSUS 1,4 ADDITION OF ''DIENOPHILES'' TO 1,3-cis,trans-CYCLOOCTADIENE

by Paul G. Gassman,[†] Herman P. Benecke, and Thomas J. Murphy[‡]

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210

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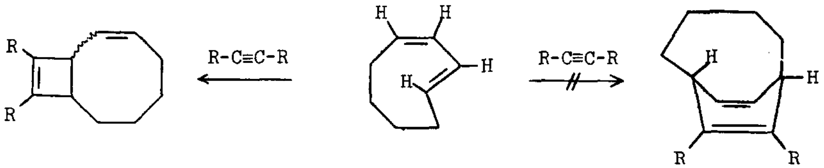
1,3-cis,trans-Cyclooctadiene (1)[1] is an intriguing diene when considered in terms of the Diels-Alder reaction. A concerted 1,4-cycloaddition of an appropriate dienophile would give the unknown bicyclic system 2. This is to be contrasted with the possible 2 + 2 addition of the dienophile to 1 which would produce 3. It should be noted that on the basis of molecular orbital symmetry arguments[2] the formation of 2 could occur via a concerted mechanism whereas a concerted thermal route to 3 is symmetry forbidden. At this time we wish to report our findings on the addition of acetylene type dienophiles to 1,3-cis,trans-cyclooctadiene.



3 1 2

In view of the report of Cope and coworkers that 1 in the presence of maleic anhydride gave polymer,[3] we first studied the reaction of 1 with dimethyl acetylenedicarboxylate (4). When equimolar amounts of 1 and 4 in benzene were heated under nitrogen at 45° for 150 hr., the 1,3-cis,trans-cyclooctadiene was approximately 65% consumed and much of 4 remained unreacted. Removal of the solvent under reduced pressure followed by column chromatography of the residue on silica gel gave 4 and a 17% yield of a fraction which consisted of a mixture of two components. Although vapor phase chromatography of the mixture indicated that the two components were present in approximately equal amounts, the separation of the two compo-

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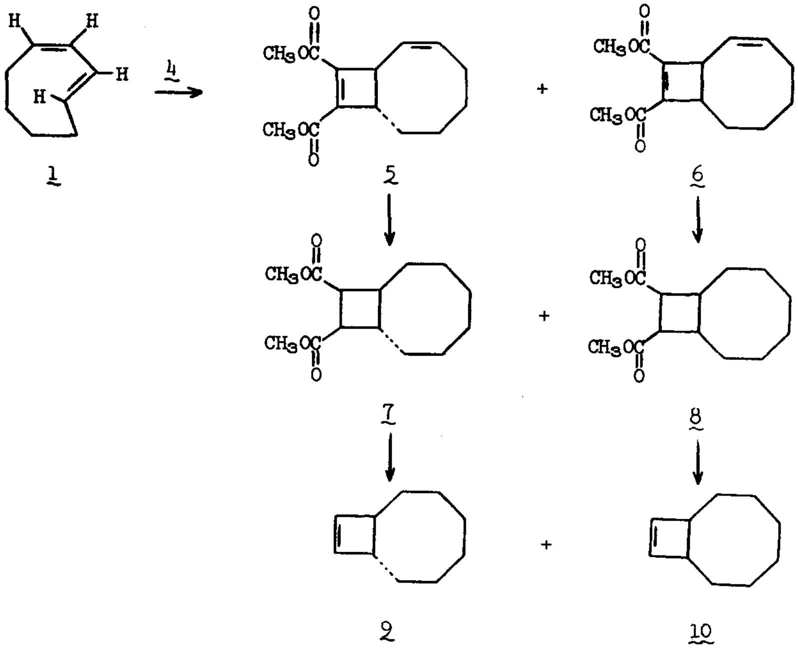
[†] Alfred P. Sloan Research Fellow 1967-1969.

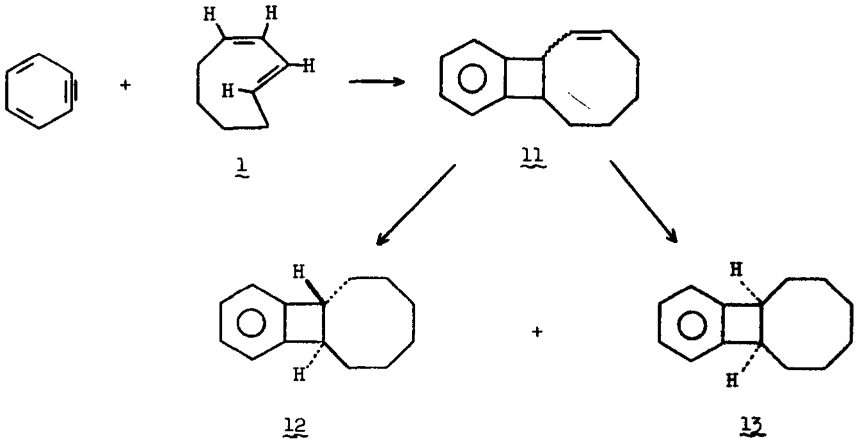
[‡] National Institutes of Health Postdoctoral Fellow, 1967-1968.

nents under optimum conditions was unsatisfactory for isolation of the pure components. The product mixture was quite unstable and underwent rapid polymerization at room temperature in the presence of air. Catalytic hydrogenation of the mixture over Pd/C resulted in the addition of two equivalents of hydrogen to 5 and 6. Vpc analysis again indicated the presence of two major components which still could not be separated on a preparative scale.[4] Saponification of the mixture of esters (7 and 8) followed by electrolytic decarboxylation[5] of the resulting mixture of acids gave 9 and 10 which were readily separated by preparative vpc. Nmr and infrared spectra of 9 and 10 were identical to those of authentic samples.[6]



The formation of 9 and 10 indicated that the hydrogenated mixture consisted of 7 and 8. The absence of any trans-cyclooctene type of olefin absorption in the infrared spectrum of the unsaturated mixture indicated that 5 and 6 were the precursors of 7 and 8 respectively.

Similarly, the addition of benzyne to 1 gave a mixture of products (11) which on catalytic hydrogenation gave 12 and 13 in 40% and 30% overall yields, respectively. Both 12 and 13 were identified via comparison with authentic samples prepared through the addition of benzyne to trans-cyclooctene.[7]



The formation of both *cis* and *trans* ring junctions in the addition of acetylene type dienophiles to 1 indicated that the mechanism involves a two-step process and not a concerted cycloaddition. By analogy to previous studies,[7,8] we believe these additions involve the formation of diradical intermediates. It is interesting to note that no evidence was found for the presence of any 2 + 4 addition reactions. Whether this is due to steric crowding in the requisite transition state for 2 + 4 addition or to some as yet unrecognized factor is not known. We are continuing our investigations in this area.

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