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DIIMIDE REDUCTION OF ALLENES

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Although the stereospecific reduction of olefins and acetylenes with the versatile reducing agent diimide is well known[1-9], there are no reports of such reduction of allenes. We now wish to report a stereospecific reduction of some cyclic and acyclic allenes with diimide. Our results are summarised in the TABLE.

TABLE

Allene	Product[(a)]	% Conversion[(b)]
1,2-Cyclononadiene	cis-Cyclononene	100
1,2,6-Cyclononatriene	cis,cis-1,5-Cyclononadiene	100
1,2-Cyclodecadiene	cis-Cyclodecene	24
1,2-Cyclotridecadiene	cis-Cyclotridecene	21
1,2-Nonadiene	cis-2-Nonene	17
3-Ethyl-1,2-pentadiene	3-Ethyl-2-pentene	16

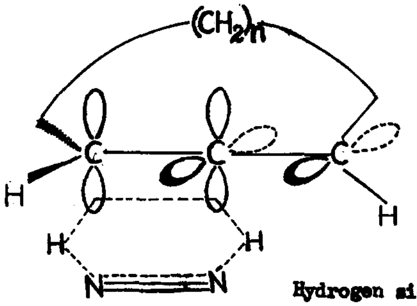
(a) The reaction products were separated, wherever necessary, by GLC and compared with authentic samples.

(b) GLC analysis.

In each case the reduction was carried out by dropwise addition of about 7 ml of hydrogen peroxide (30%) to a stirred solution of allene (0.01 mole) and 98% hydrazine (0.05 mole) in 25 ml of 95% ethanol in presence of copper ions (1 ml of 1% $CuSO_4$ solution) at 0° over a period of 30 minutes. Aliquots of the reaction mixture were removed at intervals and analysed by GLC. The GLC analysis indicated a yield of ~95% (based on the allene consumed) in each case. In no case was the isomerization of the allene or the formation of the saturated hydrocarbon observed.

Our results with cyclic allenes suggest that the preferred attack of diimide is from the least hindered side[10] (hydrogen side attack) which gives only cis-olefin.

The high degree of reactivity of the allenic linkage relative to that of an isolated double bond is illustrated by the reduction of 1,2,6-cyclononatriene. The reduction products from 1,2-nonadiene and 3-ethyl-1,2-pentadiene clearly point out that the least substituted double bond of the allenic linkage undergoes reduction as expected based on steric reasons.



Hydrogen side attack

In our view it is more likely that the sharp difference in reactivity between nine-membered cyclic allenes and the rest of the allenes may be due to the difference in strain. In fact, the strain in 1,2-cyclononadiene is reflected in its ir and nmr spectral properties which are markedly different from the other cyclic allenes[11].

The further examination of the diimide reduction of allenes is currently under study.

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