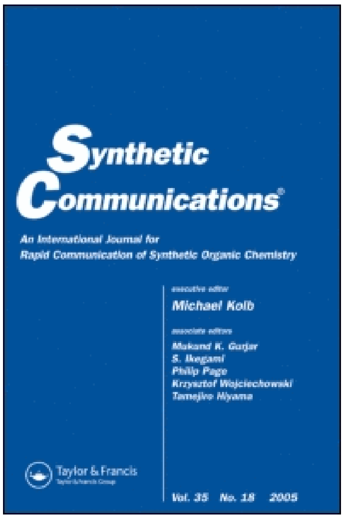

Synthetic Communications
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597304

Regiospecific Functionalization of Cyclic Allenes with Catecholeorane

V. V. Ramana Rao[a]; S. K. Agarwal[a]; D. Devaprabhakara[a]; S. Chandrasekaran[a]
[a] Department of Chemistry, Indian Institute of Technology, Kanpur, India

To cite this Article Rao, V. V. Ramana , Agarwal, S. K. , Devaprabhakara, D. and Chandrasekaran, S.(1979) 'Regiospecific Functionalization of Cyclic Allenes with Catecholeorane', Synthetic Communications, 9: 5, 437 — 442

To link to this Article: DOI: 10.1080/00397917908064174

URL: http://dx.doi.org/10.1080/00397917908064174

SYNTHETIC COMMUNICATIONS, 9(5), 437-442 (1979)

REGIOSPECIFIC FUNCTIONALIZATION OF CYCLIC ALLENES WITH CATECHOLBORANE

V.V. Ramana Rao, S.K. Agarwal , D. Devaprabhakara,
and S. Chandrasekaran*

Department of Chemistry,
Indian Institute of Technology, Kanpur-208016, India

Reaction of diborane[1] and disiamylborane[2] with cyclic allenes, resulted in the formation of a mixture of products resulting from the addition of boron at the central carbon as well as terminal carbon. Fish has reported that addition of 4,4,6-trimethyl-1,3,2-dioxaborinane to 1,3-disubstituted allenes takes place at the central carbon atom preferentially when the hydroboration was done at 130° for 35-50 h in a sealed tube.[3] The reactivity and stability of catecholborane at high temperatures which is known to provide greater stearic

---

*To whom the correspondence should be addressed control over diborane[4] prompted us to examine the hydroboration of 1,2-cyclononadiene, 1,2-cyclodecadiene and 1,2-cyclotridecadiene.

The monohydroboration of cyclic allenes with catecholborane followed by oxidation resulted in the exclusive formation of the corresponding ketones of high purity in 70-77% yield (see Table). The formation of the ketone as the one and only product clearly shows complete regioselectivity in the attack of boron at the central carbon atom of the allenic linkage. In order to examine the stereospecificity of this reaction, we did the potonolyis of the intermediate organoborane with acetic acid, which resulted in the formation of the corresponding oleins in 96-98% yield (Table). The formation of (Z)-cyclononene and (Z)-cyclodecene clearly indicate the approach of the hydroborating agent from hydrogen side. Ring side attack is not possible. In the case of 1,2-cyclotridecadiene the approach of the hydroborating agent is possible from ring side as well as from hydrogen side as evidenced by the formation of (Z)- and (E)-cyclotridecenes (76:24). These results can be explained in terms of steric requirements on a four-membered transition state.[5,6]

Work is in progress to study the monohydroboration of acylic allenes and dienes with catecholborane.

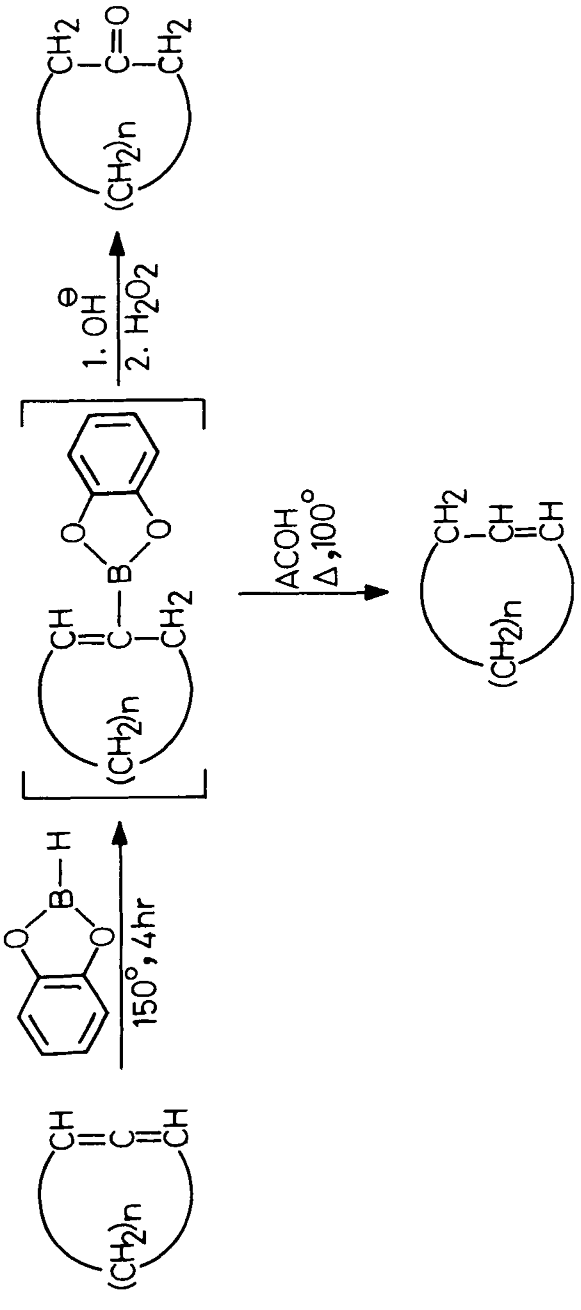
(CH2)n
CH=C=CH
O
B—H
150°, 4hr
CH=C—B
CH2
1. OH⊖
2. H2O2
CH2—C=O
CH2
ACOH
Δ,100°
CH2—CH=CH

Table: Monohydroboration of cyclic allenes with catecholborane at 150°

Allene[a]	Ketonic product[b]	Yield[c] (%)	Olefinic[d] product	Yield[e] (%)
1,2-Cyclononadiene	Cyclononanone	71	(*Z*)-Cyclononene	98
1,2-Cyclodecadiene	Cyclodecanone	77	(*Z*)-Cyclodecene	96
1,2-Cyclotridecadiene	Cyclotridecanone	73	(*Z*)-Cyclotridecene (76%)[f] (*E*)-Cyclotridecene (24%)[f]	98

a. Allenes were prepared by known procedures and thoroughly characterized prior to use.

b. Oxidation using NaOH and H_2O_2. The identity of the individual product was established by comparison of GLC retention times (carbowax 20 M, SE-30), IR spectra with those of authentic samples and m.p. of semicarbazones with reported values.

c. Isolated yield.

d. Protonolysis using glacial acetic acid at 100°. The identity of the individual product was established by comparison of GLC retention times and IR spectra with those of authentic samples.

e. Yield was calculated using internal standard.

f. Separated by preparative GLC.

EXPERIMENTAL

Hydroboration-Oxidation of Cyclic Allenes with Catecholborane: General Procedure

A mixture of allene (5 mmol) and a catecholborane (5.5 mmole) was stirred under nitrogen atmosphere at 150° for 5 h. It was cooled and the organoborane was dissolved in THF (15 ml). Excess hydride was destroyed with 1:10 mixture of water and THF at 0°. The oxidation was done by dropwise addition of sodium hydroxide (3 N, 10.2 ml, 30 mmol) followed by dropwise addition of 30% hydrogen peroxide (4.2 ml, 12 mmol) at 0°. The temperature was subsequently raised to 25-30°. After 2 h the mixture was diluted with water, after saturation with potassium carbonate, it was extracted with petroleum ether (40-60°). The extract was washed with brine, dried over anhydrous magnesium sulphate and evaporation of the solvent gave the corresponding ketone in 98% purity as analysed by GLC.

Hydroboration-Protonolysis of Cyclic Allenes with Catecholborane: General Procedure

A mixture of allene (5 mmol) catecholborane(5.5mmol) and *n*-decane (internal standard) were stirred under nitrogen atmosphere at 150° for 4 h. It was cooled and excess of hydride was destroyed with a few drops of ethyleneglycol. 5 ml of glacial acetic acid was added to the reaction mixture and stirred at 100°, extracted with pet.ether 40-60° washed with ice cold sodium hydroxide (1 N), water, dried and filtered through a bed of silica gel to get the corresponding olefin in 96-98% yield.

Acknowledgement: We thank Council of Scientific and Industrial Research, New Delhi for financial support and Dr. R. Vaidyanathaswamy, Defence Research Development and Establishment, Gwalior for IR spectra.

References

1. D. Devaprabhakara, P.D. Gardner, J. Am. Chem. Soc., 85, 1458 (1963).
2. D.S. Sethi, C.C. Joshi, Devaprabhakara, Can. J. Chem., 46, 2632 (1968).
3. R.H. Fish, J. Am. Chem. Soc., 90, 4435 (1968).
4. H.C. Brown, S.K. Gupta, J. Am. Chem. Soc., 97, 5249 (1975).
5. H.C. Brown, 'Organic Synthesis **via** Boranes,' Wiley-Interscience, New York, N.Y., 1975.
6. D.S. Sethi, G.C. Joshi, D. Devaprabhakara, Indian J. Chem., 6, 402 (1968).

Received: December 15, 1978