

264–272° dec., $\nu_{\text{max}}^{\text{KBr}}$ 3400, 3200, 1660, 1630, 1595, 1540 cm.^{-1} , $\lambda_{\text{max}}^{\text{EtOH}}$ 246, 302, 385 $\text{m}\mu$ (ϵ 5400, 3000, 10800) and was identical with natural holomycin (infrared and ultraviolet spectra, mixture m.p. determination and R_f value in paper chromatography¹⁰).

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(10) The authors wish to thank Professor V. Prelog and Dr. W. Keller for having performed this comparison.

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METAL-AMMONIA REDUCTION OF ALLENES¹

Sir:

The sodium–ammonia reduction of 1,2-cyclononadiene to *cis*-cyclononene was described recently.^{2,3} Subsequent examination of additional members—both cyclic and acyclic—of the allene family has shown the reaction to be completely general and not peculiar to strained medium-rings. Moreover, it appears to be rapid and quantitative⁴ and the product mixtures are free of rearrangement products.

The reduction of 2,3-nonadiene afforded *cis*- and *trans*-2-nonene (50/50) and less than 1% of two other substances, assumed to be *cis*- and *trans*-3-nonene. Similarly, 2-methyl-2,3-pentadiene gave rise to *trans*-4-methyl-2-pentene (48%), *cis*-4-methyl-2-pentene (34%) and 2-methyl-2-pentene (18%). 1,2-Cyclodecadiene gave only *cis*-cyclodecene while 1,2-cyclotridecadiene⁵ afforded equal amounts of *cis*- and *trans*-cyclotridecene. The synthetic utility of the method is illustrated in the reduction of readily available⁶ 1,2,6-cyclononatriene to pure *cis,cis*-1,5-cyclononadiene.⁵ Finally, the reduction of 1,2-nonadiene, the only terminal allene studied, gave *cis*-2-nonene (85%), *trans*-2-nonene (8%) and 1-nonene (6%).

Excluding for the moment 1,2-nonadiene, these reductions share one very important feature; the most hindered double bond is reduced. The attack of an electron on the allene linkage is electrophilic and therefore probably occurs at the central atom⁷ giving rise to intermediate radical-ion I. It is important to note that this species (and those formed from it) does not approach π -symmetry (*i.e.*, become an allyl radical or allyl anion) as such symmetry would leave only the substituent effects of alkyl groups to dictate the site of protonation by solvent. It is clear that I retains the configurational identity of the allene and that the direction of approach taken by the electron in the formation of I determines which double bond is reduced. This direction appears to be determined by the relative magnitude of steric interaction of the enlarged π -orbital containing the extra electron with R and R'.

(1) Supported by The Robert A. Welch Foundation.

(2) P. D. Gardner and M. Narayana, *J. Org. Chem.*, **26**, 3518 (1961).

(3) The reduction of tetraphenylpropadiene to 1,1,3,3-tetraphenylpropane [C. B. Wooster and J. F. Ryan, *J. Am. Chem. Soc.*, **56**, 1133 (1934)] is best considered in context. "The Reduction of Phenylated Olefins with Alkali Metals in Liquid Ammonia."

(4) Yields of distilled products were usually in the 80% range but no pot-residues were found; the loss is assumed to be manipulative. Analyses of alkene or cycloalkene mixtures were made by vapor–liquid chromatography on silver nitrate columns using authentic samples for retention time comparisons. Identity of products was established in some cases by comparing chromatogram charts of different runs. Product ratios described were obtained with sodium as the reductant although a brief study with lithium gave identical results.

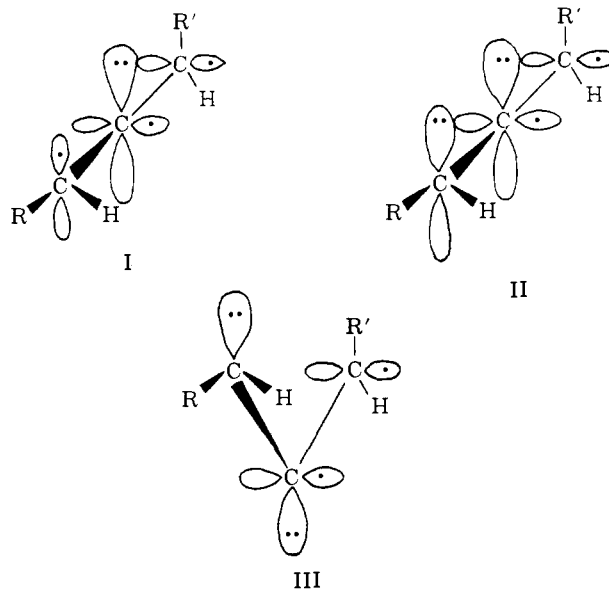
(5) This substance gave satisfactory analytical data. Its assignment of structure satisfies numerous items of chemical and physical data.

(6) L. Skätteböl, *Tetrahedron Letters*, **5**, 167 (1961).

(7) D. Devaprabhakara and P. D. Gardner, *J. Am. Chem. Soc.*, in press.

Thus, in representation I, R would be larger than R'. The attack of a second electron then precedes protonation (which would give an allyl radical) with consequent formation of dianion II. The configurational geometry of II must be as shown for reasons pointed out in the description of I; a 90° twist between the two charged atoms would give a species having symmetrical π geometry. The rehybridized dianion (III)⁸ in which coulombic repulsions are minimized at the expense of overlap energy cannot be discarded.⁹ Structure II would appear to be more consistent with the observed *cis/trans* ratios of products.

The anomalous reduction of 1,2-nonadiene suggests that terminal allenes react by a different mechanism. This possibility is under investigation.



(8) Cf. A. J. Birch and H. Smith, *Quart. Rev.*, **12**, 17 (1958), and references cited therein.

(9) Likewise, orbital geometry analogous to that in II cannot be ruled out as a representation of the dianion formed in the reduction of a disubstituted acetylene. The observed *trans* geometry⁸ of the resulting olefin would seem consistent with the type of orbital geometry shown in either II or III.

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BICYCLIC ENAMINES. I. THE FORMATION OF A SUBSTITUTED NORTRICYCLENE FROM A BICYCLIC ENAMINE¹

Sir:

It has been noted previously that the addition of a proton to an enamine takes place at the β -carbon atom to form an iminium salt² unless protonation at the β -carbon atom is sterically prohibited, in which case N-protonation takes place.^{3,4} Iminium salts possessing endocyclic double bonds^{2,4,5} and exocyclic double bonds^{6–8} have been synthesized previously. It has been found in this laboratory that protonation of certain bicyclic enamines resulted in the formation of substituted nortricyclohexenes. The production of sub-

(1) Support of this work by a Frederick Gardner Cottrell Grant from the Research Corporation is gratefully acknowledged.

(2) N. J. Leonard and V. W. Gash, *J. Am. Chem. Soc.*, **76**, 2781 (1954).

(3) C. A. Grob, A. Kaiser and E. Renk, *Chem. Ind. (London)*, 598 (1957).

(4) N. J. Leonard and A. G. Cook, *J. Am. Chem. Soc.*, **81**, 5627 (1959), previous papers and references cited therein.

(5) N. J. Doorenbos and C. L. Huang, *J. Org. Chem.*, **26**, 4106 (1961).

(6) N. J. Leonard and K. Jann, *J. Am. Chem. Soc.*, **82**, 6418 (1960), and references cited therein.

(7) G. Opitz and W. Merz, *Ann.*, **652**, 139 (1962).

(8) A. T. Blomquist and E. J. Moriconi, *J. Org. Chem.*, **26**, 3761 (1961).