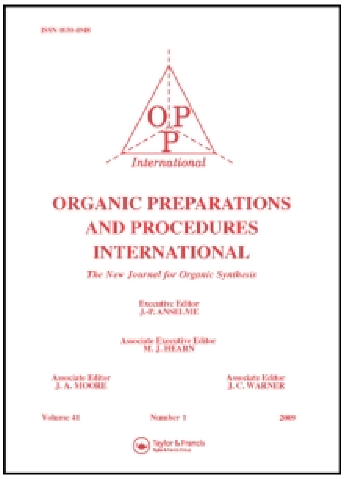

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cis - AND *trans* - CYCLOTRIDECENE

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cis- AND trans- CYCLOTRIDECENE

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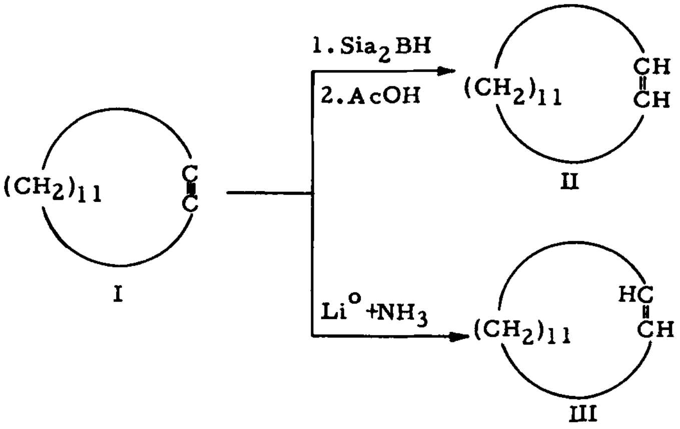
The formation of cis-cyclotridecene (II) along with its trans isomer (III) has been reported during the reduction of 1,2-cyclotridecadiene by sodium in liquid ammonia[1] and disiamylborane[2], but neither of these routes is stereospecific. The need for substantial quantities of these cyclic olefins prompted the search for a more efficient method, the results of which are the subject of this communication.

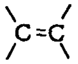
Stereospecific monohydroboration of cyclotridecyne (I)[3] with disiamylborane [Sia_2BH] followed by protonolysis provided only cis-cyclotridecene (II), whereas reduction of I with lithium in liquid ammonia gave trans-cyclotridecene (III) in better than 97% purity. The ir and

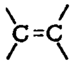


vpc retention time of each isomer were identical to those of an authentic sample. Consequently, the present procedures provide convenient and efficient preparation of cis- and trans-cyclotridecene (II and III), because of good yield in each step, isomeric purity and the ease with which each of these preparations can be carried out.

EXPERIMENTAL

cis-Cyclotridecene A mixture of 0.684 g. (18 mmoles) of pulverized sodium borohydride (Metal Hydrides Inc.), 3.36 g. (48 mmoles) of 2-methyl-2-butene (Aldrich Co.) and 20 ml. of dry diglyme (Ansul Co.) was placed in 100 ml. three-necked round bottom flask fitted with a condenser, an equilibrating dropping funnel, a low temperature thermometer, and an inlet and outlet for dry nitrogen. Hydroboration was achieved by adding 3.408 g. (24 mmoles) of boron trifluoride etherate (BDH) in 5 ml. of dry diglyme. The mixture was kept at 0 to 5^{o} with stirring over a period of 1 hr. and then 3.56 g. (20 mmoles) of cyclotridecyne (I) was added over about 5 min. The mixture was allowed to warm up to room temperature (about 3 hrs.). Having been stirred for about 3 additional hrs. at room temperature, the reaction mixture was analysed by vpc which indicated the absence of I. A small quantity of ethylene glycol was added to destroy residual hydride. About 5 ml. of glacial acetic acid was added and the mixture was left stirring overnight. It was then poured into ice-cold water, and extracted with ether. The combined extracts were washed several times with water to remove diglyme, dried over $MgSO_4$, concentrated, and distilled to give 3.2 g.

(89%) of cis- cyclotridecene (II), b.p. 107-108°/3 mm, n_D^{37} 1.4835. The vpc analysis on a 10 ft x 1/4 in. Carbowax 20 M column at 140° indicated the absence of trans isomer (III). Its ir exhibited a moderately strong band at 690 cm^{-1} assigned to cis  and had no absorption in the 960 cm^{-1} region which is characteristic of the trans isomer.[4] The identity of II was established by comparison of its ir and vpc retention time with that of an authentic sample.

trans-Cyclotridecene To a solution of 1.40 g. (0.20 mole) of lithium dissolved in about 250 ml. of commercial liquid ammonia was added 3.56 g.(20 mmoles) of cyclotridecyne (I) in 50 ml. of dry ether. The blue solution was stirred for 6 hrs. and then treated with excess ammonium chloride. After evaporation of ammonia the product was isolated by adding water to the residue and extraction of the product with ether. The combined extracts were washed with water, and dried over $MgSO_4$. After removal of the solvent the product was distilled to give 3.02 g. (84%) of trans-cyclotridecene (III), b.p. 105-108°/3 mm. The vpc analysis indicated > 97% homogenity. The ir showed a strong peak at 965 cm^{-1} characteristic of trans [4].

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