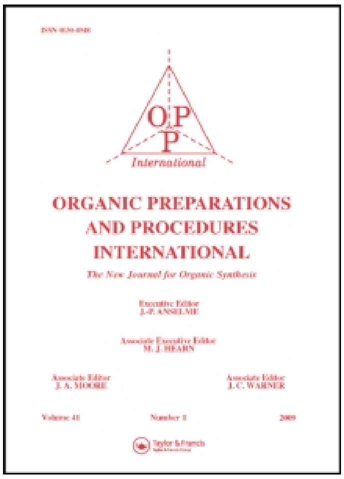

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A NEW SYNTHESIS OF NORADAMANTANE

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A NEW SYNTHESIS OF NORADAMANTANE

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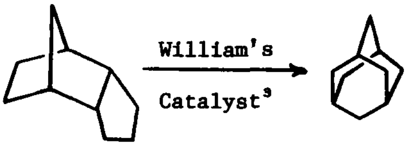
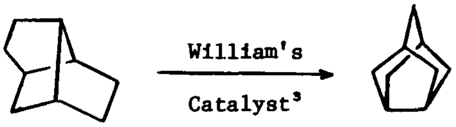
Rearrangement of polycyclic hydrocarbons with the appropriate number of atoms, in the presence of a vigorous Lewis-acid catalyst, has proved to be an extremely useful route to adamantanes (I)[1] and to noradamantane (II).[2]



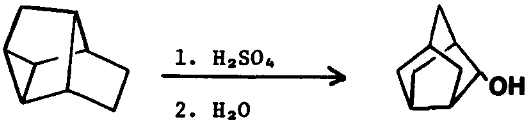
I



II

We now report an interesting new preparation of noradamantane, in which a net reduction of the precursor occurs during the transformation.

In 1967, Nickon, Pandit, and Williams[4] described a reaction in which deltacyclane (III) was converted to a noradamantol (IV) by the action of sulfuric acid.



III

IV

We have now discovered that this reaction system can be manipulated to yield any of three different compounds, including noradamantane, as the major product.[5] The purity of the noradamantane thus obtained, with no additional purification, was greater than 99% (by flame-ionization g.c.). Acceptable yields of II in this system required the presence of pentane, apparently as a hydride donor.[5]

The reduction (from C_9H_{12} to C_9H_{14}) is apparently the result of the initial protonation of III and the subsequent abstraction of a hydride ion by a noradamantyl cation after rearrangement. Since II is inert toward sulfuric acid,[5] this hydrocarbon is removed from the reaction as soon as it is formed, and is then partitioned into the pentane layer. A hydride-transfer equilibrium between various noradamantyl cations, with noradamantane as an intermediate, has been shown to occur in the absence of pentane,[5] but the details of the transfer mechanism are still unknown.

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EXPERIMENTAL

Deltacyclane[6] (10 g) in pentane (50 ml) was added to 60 ml of 96% sulfuric acid at room temperature and the mixture was stirred mechanically at high speed for two hours. (Since the reaction is heterogeneous, the stirring must be sufficiently vigorous to assure maximum contact between the immiscible sulfuric acid and pentane layers.) The layers were allowed to separate and the pentane layer was taken up with a pipette and then evaporated, leaving 3.9 g of virtually pure noradamantane. An additional 50 ml of pentane was added to the acid layer and stirring was continued for 3 hours after which the layers were separated again. This procedure was repeated three times over a 10 hour period and led ultimately to a total yield of noradamantane of about 50%. A single sublimation slight warming at full aspirator vacuum gave material of mp 203-204° that showed only one peak on flame-ionization gas chromatography and that was identical in all respects with noradamantane obtained *via* established methods.[2]

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